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# INVESTIGATIONS ON THE SULPHON-PHTHALEÏNS.

## I.—SULPHON-FLUORESCEÏN AND RELATED COMPOUNDS.

BY IRA REMSEN AND A. F. LINN.

Some results obtained by one of us (R.) and Hayes, in studying the action of resorcin upon a substance which we supposed to be ortho-sulpho-benzoic acid,[1] led us to undertake a revision of the work, in the hope that the subject might be cleared up. According to Remsen and Hayes, when resorcin and ortho-sulpho-benzoic acid are heated together, sulphon-fluoresceïn is obtained. The analyses of the product and of a barium salt obtained from it by boiling with barium carbonate, gave results which could not at the time be satisfactorily explained. On repeating the work, an observation was made at the outset which soon led to an explanation of the difficulties previously encountered. In making an analysis of the supposed ortho-sulpho-benzoic acid, it was found that a considerable amount of ammonia was given off from it on heating it with caustic potash. The substance had been prepared by heating benzoic sulphinide with concentrated hydrochloric acid in an evaporating dish on a water-bath, and had the properties ascribed to it by Remsen and Fahlberg[2] and by Brackett and Hayes.[3] Some of it further had been prepared by heating the sulphinide in a sealed tube with hydrochloric acid to 150°. In the first paper on this subject,[4] it was assumed that the action

[1] This Journal **9**, 372.
[2] Ibid. **1**, 426.
[3] Loc. cit.
[4] Loc. cit.

of hydrochloric acid upon the sulphinide takes place according to the following equation:

$$C_6H_4\begin{matrix}CO\\SO_2\end{matrix}>NH + 2H_2O + HCl = C_6H_4\begin{matrix}COOH\\SO_2OH\end{matrix} + NH_4Cl.$$

The product thus obtained was converted into the barium salt, and this into the acid potassium salt, and the latter was shown to be identical with the acid potassium salt of ortho-sulpho-benzoic, and the conclusion was drawn that the product is the free ortho-sulphonic acid. It appears, however, that this conclusion was erroneous, and that the substance is the acid ammonium salt of the acid, its formation taking place in accordance with the following equation:

$$C_6H_4\begin{matrix}CO\\SO_2\end{matrix}>NH + 2H_2O = C_6H_4\begin{matrix}COOH\\SO_2ONH_4\end{matrix}.$$

This reaction takes place in a sealed tube in the presence of concentrated hydrochloric acid at 150°. The evidence of the correctness of this view is furnished by analyses and by the preparation of the acid ammonium salt directly from the free sulphonic acid.

The nitrogen was estimated by Kjeldahl's method, the ammonia driven over being determined by means of a dilute solution of sulphuric acid of such strength that 1 cc. contained 0.0475 gram $H_2SO_4$.

In seven analyses there were found respectively 6.12, 6.25, 6.57, 6.28, 6.24, 6.55 and 6.47 per cent. of nitrogen.

The calculated percentage of nitrogen for a substance of the formula $C_6H_4\begin{matrix}COOH\\SO_2ONH_4\end{matrix}$ is 6.39.

The neutralisation experiments gave the following results:

I. 0.2149 gram substance required for neutralisation 17.6 cc. of a solution of ammonia containing 0.0009508 gram to 1 cc.

II. 0.8073 gram required 66 cc. of the same solution of ammonia.

III. 0.1938 gram required 15.9 cc. of the solution of ammonia.

The weight of ammonia required for neutralisation according to the equation:

$$C_6H_4\begin{matrix}COOH\\SO_2ONH_4\end{matrix} + NH_3 = C_6H_4\begin{matrix}COONH_4\\SO_2ONH_4\end{matrix}$$

is 7.76 per cent. of the weight of the acid ammonium salt taken. The results of the experiments correspond to 7.78, 7.77 and 7.80 per cent. respectively.

A sulphur estimation made by Liebig's method gave the following result:

0.2512 gram of the salt gave 0.267 gram $BaSO_4$.

| | Calculated for $C_6H_4<^{COOH}_{SO_2ONH_4}$. | Found. |
|---|---|---|
| S | 14.61 | 14.60 |

These results show pretty conclusively that the substance is the acid ammonium salt, and, finally, all doubt was removed by preparing the salt from free ortho-sulpho-benzoic acid by half neutralising it with a solution of ammonia. The salt obtained in this way had all the properties of the compound under investigation. A sulphur estimation gave 14.43 per cent., while the calculated percentage is 14.61.

For the sake of comparison, some of the compound was made by heating benzoic sulphinide with concentrated hydrochloric acid to 150° in a sealed tube, and the product was found to be identical in all respects with that obtained by heating the sulphinide with concentrated hydrochloric acid on a water-bath.

*Ortho-sulpho-benzoic acid,* $C_6H_4<^{COOH}_{SO_2OH}$.—The free acid was made by boiling a solution of the acid ammonium salt with barium carbonate for about two days, or until ammonia was no longer given off, filtering, exactly precipitating the barium with dilute sulphuric acid, and evaporating to a very small volume. After several recrystallisations from water, the acid forms white needles. It is very easily soluble in water, and melts at a low temperature. A thorough investigation of the acid has since been made by A. R. L. Dohme in this laboratory, and the results will be published later. They leave no question in regard to the nature of the compound.

*Action of Acid Ammonium Ortho-sulpho-benzoate on Resorcin.*

On repeating the experiment of Remsen and Hayes, the same results were obtained. When the acid ammonium salt and resorcin are heated together at 178°–185° for several hours, yellow lustrous plates appear in the liquid, and the whole mass becomes a thick, nearly solid, yellow paste. By repeatedly boiling this product with animal charcoal, all trace of color was removed and the substance was no longer fluorescent. In its pure form it is

perfectly white, and has a beautiful satiny lustre resembling that of benzoic acid. When deposited rapidly from a hot concentrated solution, it takes the form of small scales or plates. When crystallised slowly, it appears in colorless, transparent plates which are monoclinic. Analyses gave the following results:

I. 0.1054 gram substance gave 0.0735 gram $BaSO_4$ (Liebig's method).

II. 0.2736 gram substance gave 0.0011547 gram N (Kjeldahl's method).

III. 0.3813 gram substance lost 0.0305 gram $H_2O$ after heating for three to four hours at 125°–130°.

| | Calculated for $C_{13}H_{13}O_6NS + 1\frac{1}{2}H_2O$. | Found. |
|---|---|---|
| N | 4.14 | 4.22 |
| S | 9.47 | 9.57 |
| $H_2O$ | 7.99 | 8.00 |

These results show that the substance is not sulphon-fluorescein, as it was supposed to be by Remsen and Hayes, but rather that the reaction takes place between one molecule of the acid ammonium salt and one molecule of resorcin. The product is the ammonium salt of a sulphonic acid of the formula

$$(HO)_2C_6H_3.CO.C_6H_4.SO_3OH,$$

or *dioxybenzoyl-benzene-sulphonic acid*, which is analogous to the dioxybenzoyl-benzoic acid obtained by Von Baeyer[1] by heating one part of fluorescein with three parts of caustic soda. The latter reaction takes place as represented in this equation:

$$O<\underset{C_6H_3(OH)}{\overset{C_6H_3(OH)}{>}}C<\underset{O}{\overset{C_6H_4}{>}}CO + 2H_2O =$$

Fluorescein.

$$(OH)_2.C_6H_3.CO.C_6H_4.CO_2H + C_6H_4(OH)_2.$$

Dioxybenzoyl-benzoic acid. Resorcin.

The formation of the ammonium salt above described takes place according to the equation:

$$C_6H_4<\underset{SO_3ONH_4}{\overset{COOH}{}} + C_6H_4<\underset{OH}{\overset{OH}{}} =$$

$$(OH)_2C_6H_3.CO.C_6H_4.SO_3ONH_4 + H_2O.$$

The product may be regarded as derived from the acid ammonium salt by replacement of the hydroxyl of the carboxyl by the resorcin-residue, $C_6H_3(OH)_2$.

[1] Ann. Chem. (Liebig) **183**, 23.

*Dioxybenzoyl-benzene-sulphonic acid*, $(OH)_2C_6H_3 . CO . C_6H_4 . SO_3OH$.—In order to prepare the free acid, the ammonium salt was converted into the barium salt by boiling it in solution in water with barium carbonate, and the solution thus obtained was then treated with just enough dilute sulphuric acid to precipitate the barium. On evaporating the filtered solution to a small volume, the acid separated in small plates with a satiny lustre. It is extremely easily soluble in water both hot and cold. The solution is colorless, and gives no color with alkalies. When heated in an air-bath for several hours at 120° it loses water, partially fuses, and becomes yellow and finally dark brown. With alkalies, this dark brown substance gives an intense green-yellow fluorescence equal in intensity to that of fluoresceïn. It contains water of crystallisation, but owing to the fact that it is easily converted into the dark brown substance by loss of water, it is impossible to get a constant weight until this conversion is complete. The results obtained in estimating the sulphur show that the substance contains two molecules of water of crystallisation:

I. 0.1556 gram substance gave 0.1086 $BaSO_4$ = 0.0149 S (Pearson's method).

II. 0.2100 gram substance gave 0.1489 gram $BaSO_4$ = 0.02045 S (Pearson's method).

| | Calculated for $C_{13}H_{10}O_6S + 2H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| S | 9.70 | 9.58 | 9.74 |

The relation between the free acid and the ammonium salt obtained as the direct product of the action of resorcin upon acid ammonium ortho-sulpho-benzoate, was shown further by neutralising the acid with ammonia and evaporating to crystallisation, when a compound was deposited which had all the properties of the ammonium salt already described. The analyses gave the following results:

I. 0.2105 gram salt gave 0.1479 gram $BaSO_4$ = 0.020313 S (Pearson's method).

II. A determination of nitrogen by Kjeldahl's method gave 4.36 per cent. N.

III. 0.1092 gram substance lost 0.0088 gram $H_2O$ after being heated for three hours at 135°–140°.

| | Calculated for $C_{13}H_{13}O_6NS + 1\frac{1}{2}H_2O$. | Found. |
|---|---|---|
| N | 4.14 | 4.36 |
| S | 9.47 | 9.65 |
| $H_2O$ | 7.99 | 8.06 |

The *barium salt* made as above described, by boiling a solution of the ammonium salt with barium carbonate, first forms a dull red-colored solution, which on evaporation yields the salt in colored crystals. When recrystallised, however, it is obtained in large, transparent, light yellow, monoclinic plates. It is not very easily soluble in cold water, but readily in hot water. The water solution has a yellow color and shows an acid reaction. The analyses gave the following results:

I. 0.3329 gram salt gave 0.0936 gram $BaSO_4$ = 0.05503 Ba.

II. 0.2657 gram salt gave 0.0744 gram $BaSO_4$ = 0.043745 gram Ba.

III. 0.1846 gram salt gave 0.0517 gram $BaSO_4$ = 0.0303987 gram Ba.

IV. 0.2656 gram salt gave 0.0746 gram $BaSO_4$ = 0.04386 gram Ba.

V. 0.2656 gram salt, when heated for several hours at 170°–180°, lost 0.0339 gram $H_2O$.

VI. 0.3589 gram salt, when heated for several hours at 170°–180°, lost 0.046 gram $H_2O$.

| | Calculated for $(C_{13}H_9O_6S)_2Ba + 6H_2O$. | Found. | | | | | |
|---|---|---|---|---|---|---|---|
| | | I. | II. | III. | IV. | V. | VI. |
| Ba | 16.48 | 16.55 | 16.46 | 16.47 | 16.51 | ... | ... |
| $H_2O$ | 12.99 | ... | ... | ... | ... | 12.76 | 12.82 |

### *Sulphon-fluoresceïn.*

It was mentioned above that when dioxybenzoyl-benzene-sulphonic acid is heated for several hours at 120°, it is gradually converted into a dark brown substance which dissolves in alkalies, forming intensely fluorescent solutions. Von Baeyer has shown that when dioxybenzoyl-benzoic acid, or mono-resorcin-phthaleïn, as he calls it, is heated either alone or with resorcin, it is converted into fluoresceïn. It appeared highly probable, therefore, that the product obtained by heating dioxybenzoyl-benzene-sulphonic acid is the long-sought-for sulphon-fluoresceïn, and this it proved to be. The following method of preparation was found to yield entirely satisfactory results: 2 or 3 grams of the free acid are heated in a sulphuric acid bath to 185° for several hours, until the substance has acquired a dark brown color and water no longer comes off. The product is then treated with cold water and well washed. Afterwards it is dissolved in moderately concentrated caustic potash, and the solution filtered if necessary. Add dilute sulphuric

acid and wash by decantation and finally on the filter with the aid of a pump, until all traces of potassium sulphate are removed. The pure substance thus prepared has a dark red-brown color.

Sulphon-fluoresceïn is difficultly soluble in hot water and in hot alcohol, but dissolves easily in the alkalies, giving intensely fluorescent solutions, and from these solutions it is precipitated by the addition of dilute acids. In some cases, on adding dilute sulphuric acid, the substance came out in yellow flocculent masses which quickly acquired a red-brown color.

The analyses indicate that the substance has the composition represented by the formula, $C_{19}H_{12}O_6S + H_2O$, or $C_{19}H_{14}O_7S$.

I. 0.0996 gram substance gave 0.0595 gram $BaSO_4 = 0.0082$ gram S (Pearson's method).

II. 0.1029 gram substance gave 0.0639 gram $BaSO_4 = 0.00878$ gram S (Pearson's method).

III. 0.0495 gram substance, when heated for one hour at 125°–130°, lost 0.0023 gram $H_2O$.

| | Calculated for $C_{19}H_{12}O_6S + H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| S | 8.29 | 8.23 | 8.53 | ... |
| $H_2O$ | 4.66 | ... | ... | 4.65 |

Whether the water given off is "water of constitution" or of crystallisation it is impossible to determine by the aid of the facts. The simplest view is that the compound has the structure represented by the formula $C\begin{cases} C_6H_3<^{OH}_{OH} \\ C_6H_3<^{OH}_{OH} \\ C_6H_4.SO_2 \\ O— \end{cases}$, and that by loss of water it is converted into the anhydride analogous to fluoresceïn, viz. $C\begin{cases} C_6H_3<^{OH}_{O} \\ C_6H_3<^{O}_{OH}. \\ C_6H_4.SO_2 \\ O— \end{cases}$

The conversion of dioxybenzoyl-benzene-sulphonic acid into sulphon-fluoresceïn by heat, probably takes place thus:

$$2(HO)_2C_6H_3.CO.C_6H_4.SO_2OH = C\begin{cases} C_6H_4<^{OH}_{O} \\ C_6H_4<^{O}_{OH} \\ C_6H_4.SO_2 \\ O— \end{cases} + C_6H_4<^{COOH}_{SO_2OH} + H_2O.$$

When the product is dissolved in an alkali, a salt of the tetra-hydroxyl compound is then probably formed, and from this the red-brown substance which was analysed is precipitated.

According to the equation just given, ortho-sulpho-benzoic acid should be contained in the water with which the sulphon-fluorescein was first washed. On boiling this solution with animal charcoal and evaporating to a small volume, a white substance which is very easily soluble in water, and resembles in every respect the acid already described, was obtained. A barium salt was made from it by boiling its solution with barium carbonate. This salt crystallises in bunches of transparent, radiating plates which closely resemble the barium salt of ortho-sulpho-benzoic acid. On analysis it gave the following results:

I. 0.1200 gram salt lost 0.0114 gram $H_2O$ when heated for several hours at 210°; and then gave 0.0749 gram $BaSO_4$ = 0.04404 Ba.

| | Calculated for $C_6H_4<\begin{matrix}CO\\SO_3\end{matrix}>Ba + 2H_2O$. | Found. |
|---|---|---|
| Ba | 36.72 | 36.70 |
| $H_2O$ | 9.65 | 9.50 |

The investigation of sulphon-fluorescein and related compounds will be continued in this laboratory.

JOHNS HOPKINS UNIVERSITY, 1888.

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**Communications from the Chemical Laboratory of Rutgers College.**

## XV.—ON HYPOCHLOROUS ACID IN ALKALINE SOLUTION.

BY PETER T. AUSTEN.

As is well known, hypochlorous acid is a very unstable substance and decomposes on small provocation according to the formula, $2HOCl = 2HCl + O_2$.

If an excess of hydrochloric acid is present, it is at once oxidised by the oxygen that is being liberated, and chlorine alone is set free: $2HOCl + 2HCl = 2H_2O + 2Cl_2$.

Hence, in treating hypochlorites with hydrochloric acid, chlorine is to a great extent obtained, unless the solutions are kept very dilute. On the other hand, if sulphuric acid is used to liberate the hypochlorous acid, the instability of the liberated acid soon causes its decomposition in solutions that are at all concentrated.

If, however, carbonic acid is used to decompose a hypochlorite, a curious condition of opposing affinities may arise. Carbonic acid is a slightly stronger acid than hypochlorous, and hence liberates it from its salts. When so liberated, the hypochlorous acid liberates its oxygen, and hence in this condition becomes of great value as a bleacher. On this property is founded the well-known bleaching method of Thompson, who passes goods through a dilute solution of chloride of lime and then hangs them in an atmosphere of carbonic acid. In this way all danger of free chlorine and its disastrous effects on fabrics is avoided.

It occurred to me that if a solution of chloride of lime were treated with sodium bicarbonate, a curious condition of electrochemical conditions would arise; for the basic atom of hydrogen of the sodium bicarbonate must exchange with the calcium of the bleaching powder, forming sodium hypochlorite and calcium carbonate. The sodium atom of the sodium hypochlorite thus formed must again react with the basic hydrogen atom of another molecule of sodium bicarbonate, forming sodium carbonate and free hypochlorous acid.

(1). $Ca(OCl)_2 + NaHCO_3 = CaCO_3 + NaOCl + HOCl.$

(2). $NaOCl + NaHCO_3 = Na_2CO_3 + HOCl.$

$$Ca(OCl)_2 + 2NaHCO_3 = CaCO_3 + 2HOCl + Na_2CO_3.$$

I have not taken into account the calcium chloride in the bleaching powder, neither have I expressed the bleaching powder as $Ca(OH)(OCl)$, for the result in either case is the preliminary formation of sodium hypochlorite.

If the reactions are as above indicated, then we must have the somewhat paradoxical condition of a free mineral acid existing in a strongly alkaline solution. It was to be expected that when this solution of free hypochlorous acid in sodium carbonate was heated, the hypochlorous acid would decompose into hydrochloric acid and oxygen. The hydrochloric acid would act on the alkali carbonates and liberate carbonic acid. On heating, this took place. The liquid evolved gas which, after passing over caustic alkali to absorb the carbonic acid, was found to be oxygen.

A solution of sodium hypochlorite when boiled did not give off oxygen, but after passing through it a washed stream of carbonic acid, oxygen was evolved on boiling. The reaction is then,

$$2NaOCl + H_2CO_3 = 2HOCl + Na_2CO_3.$$

It is intended to try the effect of free hypochlorous acid in alkaline solution on organic substances.

I take pleasure in expressing my thanks to Mr. H. A. Smith, B. S., for efficient assistance rendered in this investigation.

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## XVI.—ON DI-AMIDO-SULPHOCYANBENZENE HYDRATE.

By Peter T. Austen.

By the action of dinitrobrombenzene on potassium sulphocyanide, dinitro-sulphocyanbenzene is formed.[1] This substance was placed in a flask with granulated tin and enough concentrated hydrochloric acid to cover the mass. On warming, an action began, which proceeded, under continued gentle application of heat, until the yellow sand had entirely disappeared and a colorless solution resulted. On evaporation of this solution, the tin salt crystallised out in transparent, shining needles, arranged in clusters of radiates about nuclei.

The salt was purified by recrystallisation from water, and analysed. The tin was precipitated as sulphide and weighed as di-oxide. The combustion was made with lead chromate, the front layer being of coarse cupric oxide.

| | Calculated for $C_6H_3(NH_3)_2SCN(HCl)_2SnCl_2$. | Found. I. | Found. II. |
|---|---|---|---|
| Sn | 27.63 | 27.27 | 27.29 |
| C | 19.67 | 19.22 | 19.19 |
| H | 2.11 | 2.34 | lost |

An attempt was next made to prepare the hydrochloride of the base. To this end the tin was precipitated by hydrogen sulphide and the filtrate evaporated. The liquid soon discolored, showing decomposition. Evaporation in a vacuum and in a current of hydrogen also failed to yield the salt, decomposition taking place in both instances. The concentrated solution obtained by

[1] Austen and Smith, this Journal **8**, 89.

evaporation in a current of hydrogen deposited a few minute crystals on standing, but repeated experiments failed to afford any appreciable amount.

Not being successful in obtaining the hydrochloride, the preparation of the free base was next undertaken. The tin was precipitated from the acid solution obtained from the reduction, and the clear filtrate evaporated to a small volume in a current of hydrogen. It was then nearly neutralised with a 10 per cent. solution of caustic soda; the neutralisation being finished with a solution of sodium carbonate. A small amount of a blue decomposition-product which had been formed during the evaporation and neutralisation, was filtered off, the liquid concentrated by boiling, and allowed to stand. A fair crop of lavender-colored crystals was obtained.

The crystals were dissolved in hot water, and boiled with a little bone-black. The nearly colorless filtrate was allowed to stand. It deposited pinkish-gray needles of about $\frac{3}{16}$ inch in length. They carbonised without preliminary fusion at 180° (uncor.). Analysis gave:

| | Calculated for $C_6H_3(NH_2)_2SCN.H_2O$. | I. | II. |
|---|---|---|---|
| C | 45.90 | 46.20 | ... |
| H | 4.92 | 5.50 | ... |
| N (absolute) | 22.95 | 23.21 | ... |
| S[1] | 17.48 | 17.45 | 17.26 |

I take pleasure in expressing my indebtedness to my assistant, Mr. Pennington Ranney, to whose skillful manipulation the success of this investigation is due.

[1] The sulphur was determined by Carius' method, by oxidation with nitric acid. The sealed glass tube was placed in an iron one, and the space between them packed with pulverised barytes, such as is sold in the paint trade. This I found fully as good, if not better than the magnesia recommended by Warren (Chemical News **58**, 155). Barytes packs easily and firmly, is very fine and very cheap. The tubes so packed are relieved of all lateral strain, and stand 280° for hours. Explosion seldom occurs. The iron tube was not capped. Should explosion occur, the iron tube acts as a gun-barrel, and, in my laboratory, discharges its contents against a brick wall with no worse result than noise, odor and a slight fume. To screw on the cap as recommended by Warren, and so often done, does not seem to me to be advisable, as a serious explosion may result when the freedom of discharge is prevented.

# ON THE BEHAVIOR OF PHENOL-PHTHALEIN WITH AMMONIA.

By J. H. Long.

The peculiar action of ammonia on phenol-phthalein was first pointed out by Beckurts, I believe, in a paper in the *Pharmaceutische Centralhalle.*[1] Soon after the experiments of Luck[2] were published, showing the great value of this substance as an indicator, it came into general use in Germany, and was even incorporated among the tests of a new edition of the German Pharmacopœia then published. Schlickum, in his Commentary on the German Pharmacopœia, 2d ed., states in one place that the behavior of litmus and phenol-phthalein in the titration of acids with ammonia water is the same, while in another place he remarks that the presence of ammonium salts interferes somewhat with the delicacy of the titration when phenol-phthalein is the indicator. Beckurts shows the error into which a number of writers had fallen in this regard, by giving a series of tests carried out with different indicators. In the following year, Flückiger[3] published experiments on the sensitiveness of phenol-phthalein, leading to the conclusion that it could not be employed with ammoniacal solutions. In the excellent papers by Thomson,[4] a similar conclusion is reached.

In the *Pharmacist*[5] I published the results of a long series of experiments on the action of phenol-phthalein, and among other points, I touched on the want of delicacy with ammonia. In that paper I offered an explanation of this behavior, suggested in part by a remark of Baeyer[6] on the formation of phenol-di-imido-phthalein, and partially confirmed this explanation by a number of experiments. Since then I have again taken up the subject, repeating the old experiments and adding new ones, which I think afford a full confirmation of my former suggestion. It is this later work which I wish to present here in detail.

When a few drops of an alcoholic solution of phenol-phthalein are added to a strong solution of soda, the deep red color which forms at first, vanishes in a short time—within a minute, if the soda

[1] 1883, p. 333.
[2] Ber. d. chem. Ges. **17**, 592. Ref.
[3] 1885, 43; also Chem. News, **51**, 160.
[4] Ztschr. anal. Chem. 1877, 332.
[4] Chem. News **47**, 125, 135 and 184.
[6] Ber. d. chem. Ges. **11**, 1297.

is sufficiently strong. The color can be restored by partial neutralisation with acids. When the indicator is added to strong ammonia solution (26 per cent.), a red color is produced which is more permanent, fading completely only after hours or days.

In this case, that is, after the *complete* disappearance of the color, addition of acid produces no change. If the acid is added before the color is fully discharged it becomes much brighter.

When phenol-phthalein is added to a very weak soda solution, the red color produced seems to be indefinitely permanent; but with weak ammonia it vanishes sooner or later, the interval between the mixing of the solutions and the disappearance of color depending on several factors, as dilution, temperature, and strength of indicator.

There are, therefore, important differences between the action of soda and that of ammonia on phenol-phthalein. If to a definite amount of a standard solution of hydrochloric acid containing a few drops of the indicator, standard ammonia solution be added, something more than the theoretical amount of the latter must be used to give the permanent red color. However, by increasing the amount of indicator added, or by cooling the solutions, the color can be obtained by nearly or quite the equivalent number of cc. of ammonia.

A similar result is obtained by adding soda solution to a solution containing, along with free mineral acid, some salt of ammonium and the indicator. The effect of temperature was shown by the following experiments. I prepared half normal solutions of hydrochloric acid and sodium hydroxide and a solution of ammonium chloride containing 100 grams in one liter. I took now 25 cc. of the acid, 10 cc. of the ammonium chloride, 65 cc. of water, and a few drops of the indicator. To the mixture, slightly less than 25 cc. of the sodium hydroxide was added, the whole was cooled to the desired temperature, and then more sodium hydroxide was run in to coloration. The results obtained at various temperatures are given in this table:

| Temperature. | cc. $\frac{N}{2}$ NaOH. | Temperature. | cc. $\frac{N}{2}$ NaOH. |
|---|---|---|---|
| 6.5 | 26.2 | 49.5 | 29.9 |
| 13.5 | 27.0 | 62.0 | 31.0 |
| 22.5 | 27.6 | 69.1 | 32.0 |
| 30.0 | 28.1 | 76.0 | 32.8 |
| 38.0 | 28.7 | | |

The final reaction was in no case as sharp as in a titration between the alkali and acid alone, but the results are close approximations. Something similar is shown in the following experiments, which disclose likewise the effects of excess of ammonium chloride. Here I employed normal solutions of hydrochloric acid, sodium hydroxide, and ammonium chloride, and for each experiment took 25 cc. of acid, a definite quantity of ammonium chloride, and added enough water to make 100 cc. In each case 1 cc. of a one-tenth per cent. solution of phenol-phthalein was added, and then caustic soda from a burette to coloration.

The solution in the beaker was kept at a temperature of 0° C., and that in the burette as near this as possible. The experiments were repeated for each mixture three times, and gave closely agreeing results, the end reactions being quite satisfactory and sharp. In the following table the mean of the results from the three tests is given:

| No. | HCl. cc. | $NH_4Cl$. cc. | $H_2O$. cc. | NaOH req'd. cc. |
|---|---|---|---|---|
| 1 | 25 | 5 | 70 | 25. |
| 2 | 25 | 10 | 65 | 25.08 |
| 3 | 25 | 15 | 60 | 25.20 |
| 4 | 25 | 25 | 50 | 25.28 |
| 5 | 25 | 30 | 45 | 25.37 |
| 6 | 25 | 50 | 25 | 25.68 |

These experiments show clearly that with the temperature sufficiently low, the disturbing action of small amounts of ammonium salts is very slight. They show also at what rate the disturbance increases with increasing amounts of ammonium chloride.

At a temperature of 20° C. I obtained the following results, working with the same solutions:

| No. | HCl. cc. | $NH_4Cl$. cc. | $H_2O$. cc. | NaOH req'd. cc. |
|---|---|---|---|---|
| 1 | 25 | 5 | 70 | 25.22 |
| 2 | 25 | 10 | 65 | 25.38 |
| 3 | 25 | 15 | 60 | 25.61 |
| 4 | 25 | 20 | 55 | 25.82 |
| 5 | 25 | 25 | 50 | 25.98 |

We find here differences in the amount of alkali required, varying between .2 cc. for the weakest solution to 1 cc. for that containing 25 cc. of ammonium chloride, which amounts to an

error of 4 per cent. In all these cases the error is so large that it could not be neglected in any kind of practical work. However, by employing a larger amount of indicator, the error can be almost entirely corrected, as shown by the following tests:

I used here 25 cc. of the acid and 5 cc. of the ammonium chloride solution at a temperature of 20° C.

1. With 2 cc. of indicator required 25.12 cc. NaOH.
2. With 4 cc. of indicator required 25.02 cc. NaOH.
3. With 6 cc. of indicator required 25.00 cc. NaOH.

By using larger amounts of the indicator, the final reaction is obtained with satisfactory sharpness.

In another series of experiments, ammonia was run into the solution containing hydrochloric acid and different amounts of the phenol-phthalein. Where but a few drops of this were taken, the end reaction could not be observed accurately; with larger amounts the reaction was sharper, but only came after addition of an excess of alkali.

1. With 25 cc. of acid and 5 cc. of indicator I used 25.57 cc. of $NH_4OH$.
2. With 25 cc. of acid and 10 cc. of indicator I used 25.28 cc. of $NH_4OH$.

In presence of alcohol the reaction was always less distinct than with water, and more alkali was required to bring it.

The above results seem to indicate that ammonia combines with phenol-phthalein, forming, to some extent, a colorless compound, besides forming a colored one as does sodium hydrate; and also that this colorless body is produced more quickly as the temperature is higher or the ammonia stronger.

I expressed the opinion in my former paper, referred to above, that the phenol-di-imido-phthalein discovered by Baeyer is the compound formed here, and that this explains the peculiar reaction.

The experiments given below seem to confirm fully this view. Baeyer[1] states that phenol-phthalein and aqueous ammonia heated to 160°–170° in sealed tubes for some hours react on each other in this way:

$$C_{20}H_{14}O_4 + 2NH_3 = C_{20}H_{16}N_2O_2 + 2H_2O.$$

The phenol-di-imido-phthalein is a colorless body soluble in alkalies without color, but which dissolves at a high temperature

[1] Ber. d. chem. Gesell. **11**, 1097.

in acids with formation of an ammonium salt and phenol-phthalein:

$$C_{20}H_{16}N_2O_2 + 2H_2O + 2HCl = C_{20}H_{14}O_4 + 2NH_4Cl.$$

I prepared the product by the following methods:

1. 3 grams of phenol-phthalein and 30 cc. of strong ammonia were heated during three hours in a sealed tube to 160° C. The tube was then opened and the contents neutralised with hydrochloric acid. This precipitated a gummy mass, which was washed thoroughly with water, and finally dissolved in 90 per cent. alcohol. The solution, after filtration through bone charcoal, was evaporated to dryness. The residue left was dissolved in a mixture of equal parts of benzene and alcohol. The solution was allowed to evaporate spontaneously, leaving a residue, which was heated to 120° C. to completely remove all traces of the solvent. The product then remained as a colorless mass of fine needle-shaped crystals.

2. 10 grams of phenol-phthalein were treated with 200 cc. of strong ammonia solution in a flask kept hot on a water-bath during fifteen hours; at the end of that time the solution was neutralised with hydrochloric acid, and an insoluble gummy mass formed was treated as under 1.

3. 10 grams of phenol-phthalein were dissolved in 200 cc. of strong ammonia water (26 per cent.) at the ordinary temperature of the room. The color formed at first disappeared in four days without application of heat. I then neutralised with hydrochloric acid, and obtained the same product as above, which was treated in the same manner.

The three substances so obtained appeared quite similar, and turned red when moderately heated in a porcelain dish, melting finally at a higher temperature. They dissolved in sodium hydroxide solution without color. When heated to 110° C. with hydrochloric acid they formed ammonium chloride and phenol-phthalein, as shown by various tests. They all dissolved in strong nitric acid with a marked yellow color, which disappeared on addition of alkali.

It is apparent, therefore, that the phenol-di-imido-phthalein can be formed at ordinary temperature as well as in a sealed tube at 160°, although the preparation of a large amount at the lower temperature would require a much longer time.

The combination between the free alkali and the trace used as

indicator in a practical titration would naturally require but a very short time at the ordinary temperature.

The rapidity of liberation of ammonia from an ammonium salt by fixed alkali depends on the temperature, and hence the very slight disturbance of the reaction with the mixed solutions in the above experiments carried out at a low temperature. Addition of sodium hydroxide seems to aid the reaction with ammonia solution, as shown by experiments in which I added the phenol-phthalein to ammonia solution and then the sodium hydroxide from a burette. With half-normal solutions the color was lost in half an hour by mixing 25 cc. sodium hydroxide, 20 cc. ammonia and .2 cc. of the indicator. Similar results were obtained with other solutions.

The above experiments show that the phenol-phthalein can be used with ammonia by taking certain precautions, and they also suggest why the behavior of this alkali was not sooner recognised. By working at a low temperature with a sufficiently large amount of the indicator, it was shown that fairly sharp results can be obtained. However, as we have other good indicators, it may never seem necessary to take these precautions.

After the introduction of the phenol-phthalein as an indicator, some time elapsed before its extreme sensitiveness was realised, and undoubtedly more was then added to a solution than is now considered necessary. Under these circumstances the difference in behavior between soda and ammonia would scarcely be noticed, and it remained for later observers, working with less of the reagent, to detect the discrepancy.

I am greatly indebted to my assistant, Mr. Mark Powers, for help in the details of the above experiments.

CHICAGO, *April* 12, 1888.

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## CONSTITUTION OF ALLYL CYANIDE.

BY CHASE PALMER.

The ease with which an allyl haloid is converted into allyl cyanide by contact with potassium cyanide at ordinary temperatures would naturally lead to the conclusion that the reaction is as follows:

$$CH_2:CH.CH_2Br + KCN = CH_2:CH.CH_2CN + KBr.$$

Allyl cyanide, however, is readily converted by alkalies into solid crotonic acid. Kekulé and Rinne[1] have also observed that, by oxidation with chromic acid, allyl cyanide does not yield formic acid, but, like crotonic acid, $CH_3.CH:CH.COOH$, it yields only acetic acid. They conclude, therefore, that a further change is involved by the introduction of the nitrile group, and that the resulting allyl cyanide has the formula $CH_3.CH:CH.CN$.

Pinner[2] retains for allyl cyanide the formula $CH_2:CH.CH_2.CN$. He assumes the first product of the alkaline action to be $\beta$-crotonic acid, $CH_2:CH.CH_2.COOH$, which takes up water directly, forming $\beta$-oxybutyric acid, $CH_3.CHOH.CH_2.COOH$, and that the latter, losing the elements of water, yields solid crotonic acid, $CH_3.CH:CH.COOH$. This ingenious explanation Pinner retains in a subsequent paper upon the same subject.[3] Hoping to learn which of the two formulas represents the constitution of allyl cyanide, I have studied the product formed by the addition of bromine to allyl cyanide.

Allyl bromide was found to furnish the largest yield of allyl cyanide, so that it was used as the source of the cyanide. As it was necessary to prepare allyl bromide, the method recommended by Grossheintz[4] was used. No data concerning the yield being available, I describe the method as I used it. 155 grams of powdered potassium bromide were mixed in a distilling flask with 75 cc. concentrated sulphuric acid, diluted with an equal volume of water. The flask was heated in an oil-bath to about 110° C., when hydrobromic acid was rapidly evolved. 50 grams of allyl alcohol were now allowed to drop slowly from a drop-funnel into the mixture. The allyl bromide distilled over through a condenser, and was collected in a receiver containing cold water. Towards the end the temperature of the oil-bath was raised to 125° C. The distillate, having been washed with water and neutralised with sodium carbonate, was separated, dried over calcium chloride, and rectified by distillation. From 50 grams of allyl alcohol 60 grams of allyl bromide were obtained.

*Allyl Cyanide.*—Since allyl cyanide cannot be made by the aid of alcohol, it was prepared by allowing allyl bromide to remain several weeks in contact with a saturated aqueous solution of potassium cyanide at the temperature of the room. 100 grams of

[1] Ber. d. chem. Ges. **6**, 386.
[2] Ibid. **12**, 2056.
[3] Ibid. **17**, 2007.
[4] Ibid. **12**, 369.

allyl bromide, 54 grams of powdered potassium cyanide, and 33 cc. of water were mixed in a bottle, which was then tightly stoppered, and allowed to remain, with frequent agitation.

At first the allyl bromide rests at the bottom of the bottle, but in about two weeks this disappears, and a light oil rises and floats on the solution. At the end of four weeks the floating oily liquid was removed, dried over calcium chloride, and fractionated. 37 grams (66 per cent. theory) of allyl cyanide were thus obtained. Considerable isonitrile was also formed. A small quantity of allyl bromide was recovered. Allyl chloride and allyl iodide, by similar treatment for a period of five weeks, gave respectively 11 per cent. and 16 per cent. of the theoretical yield of allyl cyanide.

5 grams of allyl cyanide (boiling point 116° C.) were dissolved in an equal volume of dry carbon disulphide. 11.8 grams of bromine, dissolved in five volumes of dry carbon disulphide, were allowed to drop slowly upon the allyl cyanide, which was kept cold by ice. The temperature of the cyanide solution did not rise above 10° during the process. The bromine had been distilled from sulphuric acid, and kept over lime for several days before it was used. The addition of bromine was rapid at first, but was slow towards the end. As soon as the bromine color had disappeared, the carbon disulphide was removed by distillation in a vacuum without the aid of heat, and the residue was distilled under 13 mm. pressure (oil-bath at 130°). It distilled completely below 110°, suffering partial decomposition. After standing a week in a vacuum desiccator over sulphuric acid and paraffin, it was analysed, giving a result required for dibrombutyric cyanide.

0.1965 gram substance gave 0.3270 gram AgBr.

| | Calculated for dibrombutyric cyanide. | Found. |
|---|---|---|
| Br | 70.48 per cent. | 70.79 per cent. |

This dibrombutyric cyanide is a heavy oil, having a peculiar pungent odor. Its vapor attacks the nose and eyes, causing a smarting sensation.

*Etherification of the dibrombutyric cyanide.*

A solution of 12 grams of the dibromcyanide in 20 cc. of 90 per cent. alcohol was saturated with hydrochloric acid gas at 5° C. After standing in a cold place over night, hydrochloric acid gas was again conducted through the mixture. On pouring the

mixture upon ice, a heavy oil separated. This was removed, dried over calcium chloride, and distilled in a vacuum, leaving a solid residue in the distilling flask. The oil proved to be $\alpha\beta$-dibrombutyric ether. It could not be completely purified by distillation, but it boiled in a vacuum at 104–105° C. Dibrombutyric ether obtained from $\alpha\beta$-dibrombutyric acid also boiled at 105° under the same conditions.

The solid residue in the flask was found to be $\alpha\beta$-dibrombutyramide, $CH_3.CHBr.CHBr.CONH_2$. It was washed with a little ether, and obtained pure by two crystallisations from boiling benzene. Dried to constant weight in a vacuum, it was analysed with the following result:

0.2099 gram substance gave 0.3228 gram AgBr.

| | Calculated for $C_4H_7Br_2NO$. | Found. |
|---|---|---|
| Br | 65.30 per cent. | 65.41 per cent. |

The amide is difficultly soluble in cold water; more readily in boiling water, from which it crystallises on cooling in flat plates. It is easily soluble in ether and alcohol. The amide crystallises from hot benzene in flat plates. The pure substance melts at 150°–151° C.

*$\alpha\beta$-Dibrombutyric acid.*

4 grams of the dibrombutyramide were sealed in a glass tube with 20 grams of hydrochloric acid saturated at 16° C. The tube was heated an hour in the steam-bath. On removing the tube and letting the mixture cool, ammonium chloride crystals separated out. Water was added, the mixture extracted with ether, and the ethereal solution dried over calcium chloride. On evaporating the ether, the solid residue was purified by recrystallisation from boiling benzene. It melts constantly at 85° C. Dried at 100°, an analysis gave the following result:

0.1424 gram substance gave 0.2191 gram AgBr.

| | Calculated for $C_4H_6Br_2O_2$. | Found. |
|---|---|---|
| Br | 65.04 per cent. | 65.40 per cent. |

A comparison of this acid with $\alpha\beta$-dibrombutyric acid obtained by Michael and Norton from crotonic acid,[1] shows that it is the same substance. It is very soluble in alcohol and ether. Michael and Norton found the melting point of the acid to be 87° C. when crystallised from ether.

[1] This Journal **2**, 13.

The small quantity of the acid at my disposal made the use of benzene necessary, the acid being much less soluble in benzene than in ether.

Nothing besides $\alpha\beta$-dibrombutyric ether and $\alpha\beta$-dibrombutyramide could be obtained from the dibromcyanide formed by the addition of bromine to allyl cyanide. The conclusion is therefore justified that allyl cyanide has the constitution represented by the formula $CH_2.CH:CH.CN$.

Several years ago, Würtz[1] observed that $\beta$-butylene is the principal product of the action of zinc methyl on allyl iodide in the presence of sodium:

$$2CH_2:CH.CH_2I + Zn(CH_3)_2 = 2CH_3.CH:CH.CH_3 + ZnI_2.$$

The analogous intramolecular change which occurs in the formation of allyl cyanide, $CH_2.CH:CH.CN$, from allyl bromide, $CH_2:CH.CH_2Br$, further illustrates the tendency towards a symmetrical arrangement of atoms in the molecule.

TUFTS COLLEGE, MASS., *July*, 1888.

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**Contributions from the Chemical Laboratory of Harvard College.**

## LXII.—ON THE ACTION OF SODIUM MALONIC ESTER ON TRIBROMDINITROBENZOL.[2]

BY C. LORING JACKSON AND W. S. ROBINSON.

In an earlier paper from this laboratory,[3] the preparation of tribromtrinitrobenzol and its action with ammonia and aniline were described, and the announcement was made that the study of the behavior of this very reactive body would be continued. G. D. Moore and one of us accordingly have taken up the action of sodium malonic ester upon it, in the hope of substituting for each of the bromine atoms the radical of malonic ester, $CH(COOC_2H_5)_2$, and obtaining in this way a substance which might have yielded interesting derivatives. As, however, an entirely different product

[1] Compt. Rend. **68**, 841.

[2] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[3] This Journal **10**, 283.

was the result of the reaction, it seemed wiser to study it with the much more accessible tribromdinitrobenzol, which acted in the same way, and to confine the work on the trinitro compound, which at best can be obtained only with difficulty, to those points in which the two substances showed a different behavior. In this paper, therefore, we give the results obtained up to the present time from the action of sodium malonic ester on tribromdinitrobenzol, which we are obliged to publish now, although in some respects the work is not so finished as we could wish, because the departure of one of us from Cambridge will prevent us from continuing the investigation together.

The most important of these results can be summarised briefly as follows. Sodium malonic ester, under the conditions used by us, removes from tribromdinitrobenzol only two atoms of bromine, one of which is replaced by the radical of malonic ester, the other by hydrogen, so that the formula of the product is

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2.$$

This substance shows marked acid properties, and, although of a pale yellow color itself, forms salts most of which are dark blood-red; of these the sodium salt was analysed, and its formula proved to be

$$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2.$$

The yellow copper salt was also analysed, but proved to be a somewhat complex basic salt. The bromine contained in the substance is easily removed by treatment with aniline, the product being

$$C_6H_2C_6H_5NH(NO_2)_2CH(COOC_2H_5)_2,$$

which also gives a blood-red sodium salt with a formula similar to that of the salt derived from the original substance, but the acid properties of the anilido compound are much less pronounced. When heated with strong hydrochloric acid, the bromdinitrophenylmalonic ester gives ethyl chloride and a new substance melting at 170°, but the determination of its composition must be postponed till a later paper.

*Action of Sodium Malonic Ester on Tribromdinitrobenzol.*

If an alcoholic solution of sodium malonic ester is added to tribromdinitrobenzol (melting point 192°) dissolved in ether, the first drop imparts to the ethereal solution a blood-red color, which

increases in intensity as more of the solution of sodium malonic ester is added, and the liquid contains the sodium salt of a new substance which we prepared in the following way. To an ethereal solution of a weighed quantity of tribromdinitrobenzol we added an alcoholic solution of sodium malonic ester in the proportion of three molecules of the ester to one of the tribromdinitrobenzol. The following were found to be convenient proportions: 20 grams of tribromdinitrobenzol, 16 grams of malonic ester dissolved in 100 to 150 cc. of absolute alcohol and treated with 2.4 grams of sodium as sodic ethylate. It was not necessary to add the ester gradually, and there was no perceptible evolution of heat during the reaction. The mixture was allowed to stand in a corked flask at ordinary temperatures for three or more hours, and the dark blood-red liquid thus obtained filtered from the precipitate of sodic bromide which had been deposited, acidified with dilute sulphuric acid, which changed the dark red color to pale yellow, and filtered once more to remove the sodic sulphate formed. The filtrate was then distilled on the water-bath until most of the ether had passed over, when the residue in the flask deposited, as it cooled, crystals of the new substance mixed with a large quantity of unaltered tribromdinitrobenzol. The mother-liquor from these crystals was allowed to evaporate spontaneously, and left a red or yellow oil mixed with a small additional quantity of the crystals, which were separated from it, and the oil allowed to stand in an open dish for some weeks, when it deposited an additional quantity of the crystals. The crystals, whether obtained by cooling the hot alcoholic solution, or from the oil by long standing in the cold, were purified by dissolving them in a little hot alcohol, and adding a moderately strong aqueous solution of sodic hydrate (the common laboratory solution diluted with its own volume of water), which converted the new substance into its soluble sodium salt, but left the tribromdinitrobenzol unaltered; the red solution was then poured into a large quantity of water, and the tribromdinitrobenzol removed by filtration. If the solid crystals were treated directly with the aqueous solution of sodic hydrate, the tribromdinitrobenzol was left in a form which clogged the filter very badly, whereas when an alcoholic solution was used, as directed above, no difficulty was encountered in the filtration. The red filtrate was acidified with dilute sulphuric acid, and the precipitate purified by crystallisation from hot alcohol

until it showed the constant melting-point 75°–76°. After being dried *in vacuo*, its composition was determined by the following analyses:

I. 0.2061 gram of the substance gave on combustion[1] 0.2910 gram of carbonic dioxide and 0.0602 gram of water.

II. 0.2013 gram gave 0.2827 gram of carbonic dioxide and 0.0511 gram of water.

III. 0.1975 gram gave 0.2780 gram of carbonic dioxide.[2]

IV. 0.1926 gram of substance gave 12.4 cc. of nitrogen at a temperature of 20° and a pressure of 740 mm.

V. 0.2214 gram of substance gave by the method of Carius 0.1036 gram of argentic bromide.

VI. 0.2005 gram gave 0.0937 gram of argentic bromide.

| | Found. | | | | | |
|---|---|---|---|---|---|---|
| | I. | II. | III. | IV. | V. | VI. |
| Carbon, | 38.51 | 38.30 | 38.38 | ... | ... | ... |
| Hydrogen, | 3.24 | 2.83 | ... | ... | ... | ... |
| Nitrogen, | ... | ... | ... | 7.17 | ... | ... |
| Bromine, | ... | ... | ... | ... | 19.91 | 19.88 |

These results agree about equally well with the numbers calculated for two different formulas, as appears by the following comparison:

| | Calculated for $C_6HBr(NO_2)_2C(CO_2C_2H_5)_2$. | Found Mean. | Calculated for $C_6H_2Br(NO_2)_2CH(CO_2C_2H_5)_2$. |
|---|---|---|---|
| Carbon, | 38.71 | 38.40 | 38.51 |
| Hydrogen, | 2.72 | 3.03 | 3.21 |
| Nitrogen, | 6.94 | 7.17 | 6.91 |
| Bromine, | 19.85 | 19.89 | 19.75 |

The first of these formulas, in which the two atoms of bromine removed from the tribromdinitrobenzol have been replaced by the bivalent radical $=C(CO_2C_2H_5)_2$, seems at first sight the most probable, especially since W. H. Perkin, Jr., and others have observed the strong tendency of sodium malonic ester to react in this way; but although this is the only formula we have been able to find which explains easily the removal of two atoms of bromine in this reaction, we are inclined to reject it in favor of the second one, in which one atom of bromine has been replaced by

[1] Care must be taken to heat the substance very gradually, as it shows a tendency to explode in the combustion-tube

[2] The water was lost in this analysis.

the univalent radical $-CH(CO_2C_2H_5)_2$, and the other by hydrogen, for the following reasons:

First, the formation of a sodium salt is hard to reconcile with the first formula, unless, indeed, sodic hydrate was added to it,[1] giving

$$C_6HBr(NO_2)_2OHCNa(CO_2C_2H_5)_2;$$

but our analyses of the sodium salt, given later in this paper, prove that it contains no hydroxyl, and to make this proof more convincing we prepared the salt for one of our analyses from sodic ethylate, as the radical $C_2H_5O-$, which in this case would be added instead of hydroxyl, would make a very great difference in the percentage composition of the salt; but this preparation, like the others, gave on analysis numbers corresponding to the formula

$$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2.$$

Secondly, the ease with which the sodium salt is formed, and with which it is decomposed by an acid giving the original substance, militates against the first formula, as we can hardly suppose that a ring of carbon atoms, such as must be assumed in this formula, would break when treated with an alkali, and reunite under the influence of an acid in dilute solutions. Finally, we may add that the meta position of the bromine atoms replaced deprives the first formula of any support from analogy.[2] The principal objection to the formula

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2,$$

which we adopt, is that we cannot account as yet for the formation of such a substance by the reaction of sodium malonic ester on tribromdinitrobenzol. We hope, however, that a careful study of the quantitative conditions of the reaction, and of the oil which is the secondary product, will throw light on this part of the subject; but owing to the departure of one of us from Cambridge, its further investigation must be postponed till next autumn.

The yield was far from satisfactory; 14 grams of tribromdinitrobenzol after treatment with 12 grams of malonic ester and 1.7 gram of sodium, as described above, giving only 4.3 grams of the bromdinitrophenylmalonic ester instead of the 14 grams required, if the whole of the tribromdinitrobenzol was converted into the new

[1] Wislicenus, Ann. Chem. **242**, 23.

[2] Compare J. Stanley Kipping, Ber. d. chem. Ges. **21**, 32.

substance, that is, 30.7 per cent. of the theoretical yield. A large amount of the tribromdinitrobenzol was recovered, however, amounting to 5.5 grams, or 39.3 per cent. This leaves 30 per cent. unaccounted for, which probably remains dissolved in the oil deposited by the alcoholic mother-liquors; but that the dissolved substance is bromdinitrophenylmalonic ester admits of great doubt, as we have not succeeded in obtaining any considerable quantity of this substance from the oil by treatment with aqueous sodic hydrate. This point will be investigated more thoroughly hereafter. We have tried several modifications of the process, in hopes of improving the yield, but none of them have given satisfactory results; if, for instance, the proportion of sodium malonic ester is increased in order to bring more of the tribromdinitrobenzol into the reaction, any gain from this cause is more than compensated by the larger amount of the product taken up by the greater quantity of oil, which is only in part deposited on long standing. Nor was the yield increased by longer standing, or by boiling the materials with a reverse condenser; in this latter case the product came down in an oily form, and with, if anything, rather a smaller yield, was much harder to purify.

*Properties of the Bromdinitrophenylmalonic Ester,*

$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$.

The substance crystallises in pale yellow flattened needles, or long plates terminated by a single plane, which forms with the sides angles not very far from 90°, but distinctly obtuse and acute. It melts between 75° and 76°, and shows a tendency to explode at high temperatures, so that the heat must be applied carefully when making a combustion of the substance. It is not very soluble in cold alcohol, but freely in hot, more soluble in methyl than in ethyl alcohol, freely soluble in ether, benzol, or glacial acetic acid, even more so in chloroform; moderately soluble in acetone or carbonic disulphide, nearly insoluble in ligroine or water. Strong sulphuric acid in the cold has little action on it, although perhaps a small quantity dissolves; on warming the mixture, complete solution takes place, and addition of water precipitates a solid, which seems to consist principally of unaltered bromdinitrophenylmalonic ester mixed with a small amount of a substance with a higher melting point, probably the compound formed by the action

of concentrated hydrochloric acid in sealed tubes (see page 104). Nitric acid, either strong or fuming, dissolves the bromdinitrophenylmalonic ester in the cold, but does not produce any change of color. In this respect it differs markedly from the corresponding trinitro compound. If the acid solution is warmed, decomposition seems to take place.

The bromdinitrophenylmalonic ester possesses well-marked acid properties, as was to be expected, since it contains a hydrogen atom standing between the two carboxyls of the malonic ester and a phenyl, which, as Victor Meyer[1] has shown, frequently exercises a negative influence, much heightened in this case by the presence of the two nitro groups. Sodic hydrate in either aqueous or alcoholic solution at once converts it into a soluble red sodium salt, and the same salt is formed by an alcoholic solution of sodium malonic ester, by sodic carbonate dissolved in water, or by acid sodic carbonate mixed with very dilute alcohol. The aqueous solution of the salt is, however, entirely decomposed by carbonic dioxide, the original substance being precipitated. An aqueous solution of the sodium salt prepared by treating an excess of the original substance with a solution of sodic hydrate, gave precipitates with salts of all the common metals except those of the alkalies. Most of these precipitates were red, and among them the following were especially characteristic:

Baric, strontic, or calcic chloride, dark brick-red.

Magnesic sulphate, rust color.

Zincic acetate, dark chrome-orange.

Basic plumbic acetate, very dark brick-red.

The neutral plumbic acetate gave a yellow precipitate, which turned white when in contact with an excess of lead salt.

Cupric sulphate, dark golden yellow.

Ammonic hydrate also dissolved the substance with a red color, but the salt was decomposed on trying to evaporate off the excess of ammonia on the water-bath, leaving a whitish residue, which seemed to consist principally of the original substance, with a small amount of decomposition product. The substance is in fact easily decomposed by either ammonic or sodic hydrate, and our rather unsatisfactory observations on these reactions will be found on page 104. The sodium salt boiled under a reverse condenser

[1] Ber. d. chem. Ges. **20**, 534; **21**, 1991 et seq.

with ethyl bromide in alcoholic solution, passed from red through purple, bluish green, green and brown to reddish yellow; sodic bromide was formed, and the other product was an oily substance, which solidified after some time. It will be studied later. The bromine atom in the bromdinitrophenylmalonic ester seems to be removed with comparative ease. Up to this time, we have studied its behavior in this direction only with aniline (see page 102).

*The Sodium Salt*, $C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2$.

This substance was prepared by dissolving some of the bromdinitrophenylmalonic ester in alcohol and adding a little sodic hydrate, care being taken that the hydrate was not in excess; a little ether was then added, and the mixture evaporated rapidly in a small beaker sunk throughout its whole length in the water-bath. The ether vapor kept the air from coming in contact with the liquid while the alcohol was being heated to its boiling point. The residue, after all the alcohol had evaporated, was extracted with benzol to remove the excess of the ester, and then dried by gentle warming and standing *in vacuo* over paraffin and sulphuric acid. These precautions were adopted to avoid the contamination of the substance with the carbonic dioxide of the air. The same substance was obtained when sodic ethylate was used instead of sodic hydrate, and Analysis III was made with a sample prepared in this way.

I. 0.1950 gram of the substance ignited with sulphuric acid gave 0.0324 gram of sodic sulphate.

II. 0.1354 gram gave 0.0216 gram of sodic sulphate.

III. 0.1943 gram gave by the method of Carius 0.0838 gram of argentic bromide, and the filtrate gave 0.0330 gram of sodic sulphate.

IV. 0.2148 gram gave 14.3 cc. nitrogen at a temperature of 25° and a pressure of 759.6 mm.

| | Calculated for $C_6H_2Br(NO_2)_2CNa(CO_2C_2H_5)_2$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Sodium, | 5.39 | 5.38 | 5.16 | 5.50 | ... |
| Bromine, | 18.74 | ... | ... | 18.35 | ... |
| Nitrogen, | 6.55 | ... | ... | ... | 7.42 |

The results of these analyses show that the substance is the normal salt, containing but one atom of sodium, and the important bearing of this point on the determination of the formula of the

bromdinitrophenylmalonic ester has been discussed already. (See page 97.)

*Properties.*—The salt forms a dark blood-red powder, easily soluble in water, alcohol, or ether. From a solution containing much sodic hydrate, the salt can be extracted with ether; but pure water, on the other hand, extracts the salt from its ethereal solution. Its aqueous solution is decolorised by carbonic dioxide, bromdinitrophenylmalonic ester being precipitated.

The *copper salt* seemed from its appearance to promise excellent results on investigation, and was accordingly prepared as follows. An alcoholic solution of the bromdinitrophenylmalonic ester was treated with a small quantity of sodic hydrate, taking care that the ester was in large excess, and then poured into a volume of water sufficient to precipitate all the unaltered ester; after filtering, an alcoholic solution of cupric chloride was added, and the precipitate washed first with 50 per cent. alcohol, then with water, and finally once with hot alcohol; it was then dried *in vacuo*. It is not necessary to protect the salt from contact with the air during its preparation, as it is not perceptibly affected by carbonic dioxide. It gave the following results on analysis:

I. 0.2052 gram of the salt was treated according to the method of Carius and gave 0.0844 gram of argentic bromide. The filtrate was freed from argentic nitrate, and the copper precipitated by electricity from a sulphuric or nitric acid solution, giving 0.0197 gram of copper.

II. 0.2073 gram treated in the same way gave 0.0864 gram of argentic bromide and 0.0198 gram of copper.

III. 0.1455 gram gave 0.0138 gram of copper.

| | Calculated for $HOCu_3[C_6H_2Br(NO_2)_2C(CO_2C_2H_5)_2]_3$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Copper, | 9.36 | 9.60 | 9.55 | 9.48 |
| Bromine, | 17.70 | 17.50 | 17.74 | ... |

From these results it would appear that the substance is a basic salt, or, at least, that it is not the normal salt, and in spite of its very promising appearance is not fitted to throw light on the nature of the original substance. We have not thought it worth while, therefore, to examine it more carefully. We may add that the salt changes color from a lighter to a darker yellow soon after it is prepared, which we are inclined to ascribe to the conversion of

$$ClCu_3[C_6H_2Br(NO_2)_2C(CO_2C_2H_5)_2]_3$$

into the corresponding hydroxyl compound by the action of the water in which it is suspended.

*Properties.*—The copper salt forms an obscurely crystalline precipitate of a golden yellow color, with a very slight greenish tinge. It is essentially insoluble in water, alcohol, or ether, and is a comparatively stable substance, as it seems to be unaltered by exposure to the air or by heating to 100°. Strong nitric acid, even in excess, decomposes it, setting free the bromdinitrophenylmalonic ester.

*Anilidodinitrophenylmalonic Ester,*

$C_6H_5NHC_6H_2(NO_2)_2CH(COOC_2H_5)_2$.

This substance was made by mixing the bromdinitrophenylmalonic ester with aniline in the proportion of one molecule of the ester to two of the base. The solid becomes yellow almost immediately, and the action has come essentially to an end after the mixture has stood for a few minutes in the cold. As a measure of precaution, however, we always heated it gently for a few minutes, to make certain that all the bromine had been removed. The product was purified by crystallisation from alcohol, until it showed the constant melting point 118°, dried at 100°, and analysed.

I. 0.2104 gram of the substance gave on combustion 0.4262 gram of carbonic dioxide and 0.0903 gram of water.

II. 0.1886 gram of the substance gave 16.9 cc. of nitrogen at a temperature of 22° and a pressure of 766.6 mm.

| | Calculated for $C_6H_2(NHC_6H_5)(NO_2)_2CH(CO_2C_2H_5)_2$. | Found. I. | II. |
|---|---|---|---|
| Carbon, | 54.68 | 55.24 | ... |
| Hydrogen, | 4.56 | 4.77 | ... |
| Nitrogen, | 10.07 | ... | 10.24 |

*Properties.*—The anilidodinitrophenylmalonic ester forms flattened needles terminated by one or two planes, which form much more oblique angles with the sides than those which appear in the bromdinitrophenylmalonic ester. It is also found occasionally in star-shaped groups of needles, has a bright yellow color, and melts at 118°. It is only slightly soluble in cold alcohol, much more soluble in hot, but not freely even in this. More soluble in methyl than in ethyl alcohol; soluble in ether, or in carbonic disulphide; freely soluble in benzol, glacial acetic acid, or acetone, very freely

in chloroform; essentially insoluble in water or ligroine. The best solvent for it is alcohol. Concentrated hydrochloric acid does not dissolve or act on it in open vessels, either hot or cold. An aqueous solution of sodic hydrate acts on it in the cold only very slowly and imperfectly, but gives a red solution when boiled with it. In alcoholic solution, sodic hydrate converts it into a red soluble salt; the anilido compound therefore still possesses acid properties, but these are much less marked than in the corresponding bromine compound; the negative influence of the dinitrophenyl therefore has been partly neutralised by the introduction of the basic aniline radical $C_6H_5NH$.

*The Sodium Salt*, $C_6H_2(C_6H_5NH)(NO_2)_2CNa(COOC_2H_5)_2$.

This substance was formed in the same way as the sodium salt of the bromdinitrophenylmalonic ester; that is, by treating an alcoholic solution of the substance with alcoholic sodic hydrate not in excess, evaporating to dryness with a little ether on the water-bath, and extracting the excess of the ester with benzol. It was dried at 100°, and analysed.

0.1180 gram of substance gave 0.0194 gram of sodic sulphate.

| | Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2CNa(CO_2C_2H_5)_2$. | Found. |
|---|---|---|
| Sodium, | 5.24 | 5.32 |

*Properties.*—It resembles the sodium salt of the bromdinitrophenylmalonic ester closely in appearance and solubility, but is of a somewhat lighter red. Its solution is decomposed when treated with carbonic dioxide.

## *Experiments on the Saponification of Bromdinitrophenylmalonic Ester.*

In taking up this subject we considered it necessary to study the action of alkalies on the ester, although, owing to the ease with which the nitro groups are attacked, we had little expectation of reaching satisfactory results. In this we were not deceived, but we think it best to give a brief account of these experiments before describing our more successful work with strong hydrochloric acid in sealed tubes.

A solution of sodic hydrate in water, if boiled with the brom- or anilidodinitromalonic ester, gave a brownish red solution, from which acids precipitated nothing; but after acidification, and

extraction with ether, an unpromising oil was obtained in very small quantity. Cold alcoholic sodic hydrate with the anilido compound gave a somewhat more promising result, but in this case also most of the substance seemed to be decomposed. The bromine compound, after standing for two weeks with ammonic hydrate at ordinary temperatures, was converted into a similar brown solution, which on acidification gave a resinous brown precipitate and a yellow filtrate, from which ether extracted a substance melting above 200°, ammonic bromide being formed during the process. This is the only one of these products which seems worth further investigation.

### *Action of Hydrochloric Acid.*[1]

When the bromdinitrophenylmalonic ester was heated with strong hydrochloric acid in a sealed tube to 140°–145°, it was decomposed, and upon opening the tube a gas was given off in tolerable quantity, which burnt with a green-bordered flame, and was without doubt ethyl chloride. About one gram of the substance and 20 cc. of common strong hydrochloric acid were used in each tube, and the temperature should not be allowed to go above 150°, as in this case an impure product was the result. If proper care was used in the heating, the tube contained crystals, or a clear liquid from which crystals were deposited after the pressure was relieved; these were filtered out and the filtrate thrown away, as it gave almost no residue on evaporation, and no extract when shaken with ether.

The crystals were purified by crystallisation from dilute alcohol (three parts of water to one part of alcohol). If the temperature was kept below 150°, the product was nearly pure, as it came from the tube; but if it had risen above this point, a small quantity of a lower melting substance was formed, which it was almost impossible to remove with dilute alcohol. In this case the best plan was to dissolve the substance in chloroform, when the impurity separated at first as a pasty mass, leaving the principal product in solution, which after one crystallisation from dilute alcohol showed the constant melting point 170°.[2]

[1] All our work on this part of the subject must be regarded as preliminary.

[2] Later work has shown that it is essentially impossible to purify the substance by crystallisation from dilute alcohol, and that when pure it melts at 177°, not at 170°. We have withdrawn, therefore, from this paper the analyses made last year of the substance melting at 170°, and prefer to make no statement about the composition of the substance, until the investigation of it, upon which we are now engaged, has come to a conclusion.

*Properties.*—The substance crystallises from dilute alcohol in yellowish white narrow plates, sometimes half a centimeter in length, which are made up of needles attached to another needle acting as a midrib at very acute angles, giving an exact imitation of a feather, or more commonly of one side of a feather; this form is very characteristic, and, when not so well developed, the substance can be recognised by the formation of narrow plates, usually smooth on one side and rather irregularly serrated on the other or upon the ends. The plates often occur in radiating groups, the members of which form very acute angles with each other. From methyl alcohol or ether it crystallises in very slender needles, much branched at very sharp angles, often forming circular groups resembling certain seaweeds. It melts at 170°, is not very soluble in cold alcohol, freely in hot, more soluble in methyl than in ethyl alcohol, freely soluble in glacial acetic acid or acetone, tolerably soluble in ether, slightly soluble in benzol either cold or hot, or in carbonic disulphide; slightly soluble in cold chloroform, more soluble but not freely in hot, nearly insoluble but not quite so in cold water, more soluble but still very slightly in hot, essentially insoluble in ligroine. The best solvent for it is chloroform, or a mixture of alcohol and water. Its behavior with alkalies is very characteristic. If a drop of an aqueous solution of sodic hydrate is added to the substance dissolved in alcohol, the solution takes on a dark but brilliant Prussian green color. This solution becomes colorless on addition of hydrochloric acid, but turns green again on addition of sodic hydrate. The green alcoholic solution, if allowed to evaporate spontaneously, leaves a brownish yellow residue, and a solution of the same brownish yellow color is obtained if an *excess* of sodic hydrate is added to the original substance. If the yellow solution, in whichever way prepared, is acidified with hydrochloric acid, it loses its color, and oil-drops are precipitated, which solidify in time. These dissolve in sodic hydrate with a brownish claret[1] or pale magenta color, which is unaltered by dilution with water, but turns green on addition of alcohol. The substance melting at 170° is not affected by an aqueous solution of sodic carbonate. The further study of these interesting reactions has been broken off by the summer vacation, but will be continued in this laboratory in the autumn.

[1] A somewhat similar change of color was observed during the action of ethylbromide on the sodium salt of the bromdinitrophenylmalonic ester.

# THE RATES OF TRANSFERENCE AND THE CONDUCTING POWER OF CERTAIN SILVER SALTS.[1]

By Walther Nernst and Morris Loeb.

## 1. *Introduction.*

Whenever a current of electricity is passed through a conductor of the second class, under such conditions that the composition of the solution is not changed, as when a current passes between electrodes of the same metal in a solution of a salt of that metal, curious changes of concentration appear. This was noticed by many scientists, but it was reserved for Hittorf to investigate these changes quantitatively and to advance a plausible and exhaustive hypothesis of their causes. His work constitutes one of the classics in physics; but as it is not, perhaps, so generally known to chemists, a short explanation of his hypothesis may be a not inappropriate introduction to our paper. Taking the example already cited, it is, of course, a familiar principle, that in a given interval the same amount of metal is dissolved from the positive electrode as is deposited upon the negative electrode. If we were to assume that the ions of the electrolyte were incapable of moving independently of each other, the changes in concentration at the two electrodes could only be counterbalanced by the slow process of diffusion, and we should find a deficit in the liquid around the negative electrode corresponding to the amount of metal deposited upon the latter, while all the metal yielded up by the positive electrode would be found in its immediate surroundings. This is, of course, an untenable assumption. Supposing, on the other hand, that only the negative ions were immovable, while the positive ones could travel across the liquid as fast as required to supply the places of those disappearing upon the negative electrode: the liquid would be homogeneous at all moments, and there would be no concentration nor dilution around the electrodes. We cannot, however, assume that the negative ions are immovable, everything showing that they move toward the cathode just as well as the positive ones do toward the anode. If both move

[1] Abbreviated translation from the paper appearing in the Zeitschrift für physikalische Chemie **2**, 948, made for this Journal by one of the authors.

with equal rapidity, as was tacitly assumed before Hittorf, a little reflection will show that the liquid about the cathode will lose just half as much metal as is deposited upon the electrode, while half the metal given up by the anode to the surrounding liquid will have been transferred toward the cathode. Hittorf's laborious analyses proved that none of these three possibilities was fulfilled. The relation between the changes in concentration and the amount of metal transferred from one electrode to the other proved conclusively that the two classes of ions did not move with equal rapidity; and he showed how this ratio provided a measurement of the share of each class in the total movement. For any salt, the ratio of the weight of the metal deposited to the amount of metal lost by the fluid around the cathode (or its equivalent, the amount gained by that around the anode) represents the share of the negative ion, the anion, in the total movement.

Hittorf has had few followers in these investigations,[1] as the difficulties of experiment were discouraging. Analytical accuracy demanded the use of concentrated solutions, or of bulky and cumbrous apparatus, while it was especially desirable to study dilute solutions, and to use apparatus which was not subject to such disturbances as variations of temperature, osmose, and the jars unavoidable during mechanical handling produce. Considerations which will be explained later led us to attempt the acquisition of fresh material, especially with reference to highly dilute solutions. We found that we could do this by studying certain silver salts, mainly organic; and we were led to this choice firstly because silver is the only monovalent metal which furnishes a satisfactory electrode—a matter of some moment for our subsequent work; secondly, because its salts are readily obtained in the needful state of purity; finally, because Volhard's beautiful method of titration[2] enabled us to perform the necessary analyses with great ease and extreme nicety. We also availed ourselves of the opportunity for studying the effects of temperature and concentration upon the velocity of the ions of these salts, because one of us[3] has recently shown how important a part is played by these factors in the kinetics of solutions.

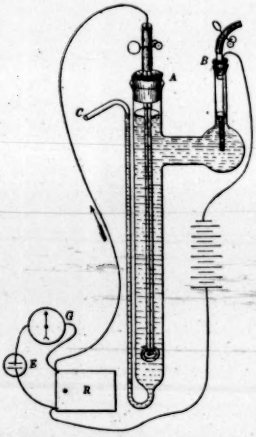
[1] The following list includes all the literature: Hittorf, Ann. der Phys. Pogg. **89**, 177, **98**, 1, **103**, 1, **106**, 337; G. Wiedemann, ibid. **99**, 177; Weiske, ibid. **103**, 466; Kuschel, Ann. der Phys. Wied. **13**, 289; Kirmis, ibid. **4**, 503; Lenz, Mém. Ac. Petersbourg **30**, 1882.

[2] Volhard, Ann. Chem. (Liebig) **190**, 1.

[3] Nernst, Zeitschrift für physikalische Chemie **2**, 613.

### 2. *Apparatus for the Determination of the Rate of Transference.*

In this apparatus we wished to avoid the use of membranous diaphragms, and to minimise the internal resistance, necessarily large by reason of our very dilute solutions, so as to keep the necessary duration of an experiment within reasonable limits. After various failures we finally hit upon a form whose simplicity is likely to recommend it in similar cases. As shown in the accompanying drawing, it is seen to resemble the Gay-Lussac burette, but with the addition of a short side-tube of the same bore as the main tube. This side-tube ends in a bulb, and upon this is set a narrower vertical tube, through which the negative electrode—a cylindrical roll of silver foil fastened to a silver wire—can be let down into the bulb. This works as a sort of pocket, by which masses of the spongy precipitated silver that may become detached from the electrode are prevented from stirring up the body of the solution. The anode consists of a silver wire rolled into a spiral at the lower end. It is introduced through *A*, and reaches to the bottom of the main tube. In order that the current may enter the liquid only at the spiral, the straight part of the wire is covered with a capillary of very thin glass, which can be closed around the wire by fusion, in spite of the difference in their coefficients of expansion. The openings *A* and *B* are closed with corks that are traversed by short glass tubes. Of these, the tube at *A* allows free passage to the wire of the electrode. The wall of the tube at *B* is pierced by a platinum wire, which serves to suspend the cathode and to connect it with the conductor of the battery. Thus *A* can be closed by the compression of a bit of rubber tubing drawn over the wire and glass tube, or air can be sucked or blown through a rubber tube connected with *B*, without disturbing the electrodes.



In experimenting, such an apparatus would first be weighed with its electrodes and stoppers, but without the rubber tubing. The latter was hereupon put in position, *A* was closed with a pinch-cock as just indicated, and air was drawn out at *B* while the nozzle *C* was dipping under the surface of the solution to be used. By this process, the main- and side-tubes were filled up to the level of the top of the latter; the sizes of apparatus we employed contained 40 and 60 cc. respectively. The nozzle was now likewise closed with a rubber cap, and the whole apparatus suspended in such a fashion, in one of Prof. Ostwald's thermostatic water-baths,[1] that the nozzle protruded over the rim, while the liquid was entirely within the water-bath. After it had acquired the temperature of the bath, the circuit was closed. As soon as the electrolysis was concluded, the nozzle was opened and suitable portions of the liquid were filled into tared vessels, by blowing steadily through *B*. These portions were weighed and analysed. The portion remaining in the apparatus was estimated by the latter's gain in weight, and likewise analysed. Provided there has been no mixing through diffusion and convection during the electrolysis, the first portion taken from the apparatus, if the liquid is properly divided, will consist of the stratum around the anode, which has become more concentrated, and of a sufficient quantity of the unaltered middle layers to insure a rinsing of the adhering parts of the lowest stratum. The succeeding portions being composed wholly of the middle layers, must show an unaltered composition, while what is left in the apparatus includes the diluter strata about the cathode. To prove the reliability of our experiment, we must find in the first place that the middle layers had remained unchanged, and secondly, that the gain of the lowest layer exactly counterbalanced the loss of the highest, for the mean composition of the whole liquid undergoes no change. After finding that the first condition was invariably fulfilled, we saved time by giving up the separate examination of the middle layers, and divided the whole liquid into two nearly equal portions. It frequently happened that, during the electrolysis, the electrolysed silver would grow out from the bulb along the wall of the horizontal tube. In such cases the circuit was broken before the silver had reached the main tube; other-

[1] As described recently by Prof. Ostwald, Ztschr. phys. Chem. 2, 565.

wise, we disconnected whenever we estimated that a sufficient change of concentration had taken place to give the most reliable results.

The analyses were performed, as already intimated, by titration with a solution of ammonic sulphocyanate, the standard of which (about $\frac{1}{100}$ normal) was ascertained by frequent comparison with an argentic nitrate solution of known strength, occasional gravimetric determinations of which gave absolutely constant results. We claim for the titrations an error well within $\frac{1}{30}$ cc. (= 0.038 milligrams Ag), each end-reaction being observed twice, as 1 cc. of a $\frac{1}{100}$ normal solution of argentic nitrate was added from a pipette, after the first appearance of the characteristic tint, and the titration repeated.

The ratio we are seeking to determine requires, besides the data of the change in concentration, the weight of the silver which has been actually deposited upon the cathode, in the same interval of time. This would most naturally be determined by a silver voltameter placed in the same circuit with the apparatus. But as the examination of dilute solutions often necessitated the deposit of less than 20 milligrams in all, and the silver is deposited in such a form upon the voltameter that it is difficult to weigh it without a slight loss, we found it to be more advantageous to determine the quantity of electricity which traversed the apparatus by galvanometric measurement. A resistance-box was introduced into the circuit for this purpose (see figure), to the extremities of which a second circuit was connected, containing a Clark's cell and a galvanometer with direct reading. The Clark's cell being introduced in the proper direction, it is well known that a suitable resistance $R$ may be introduced by means of the box, which will put the galvanometer at rest at the $O$ point; when this is effected, we have for the electrical intensity of the main current $i = \frac{E}{R}$, $E$ denoting the electromotive force of the standard Clark's cell. As the intensity of the current changed but little and very gradually during the four or five hours which were usually occupied by an electrolysis, we were satisfied with making this measurement, which required but a few seconds' attention, every ten minutes. The total amount of electricity could then be integrated with sufficient certainty.

Special experiments showed that, when resistance-box and

Clark's cell were at a temperature of 18° C., the quantity $f$ of precipitated silver could be found by the formula,

$$f = \frac{\tau}{r} 92.69,$$

where $\tau$ represents the duration of the electrolysis in minutes, while $r$ denotes the resistance which would have been necessary to keep the galvanometer at $O$, provided that amount of electricity which actually passed through the apparatus had done so in a current which remained constant throughout this interval. Whenever the resistance-box and the cell were at any other temperature, $t$, the above expression must be multiplied with the factor $1 - 0.0012(t - 18)$. This coefficient of temperature, 0.0012 is derived from that of the cell, —0.0008, and that of the box, + 0.0004.

Our battery consisted of 38 Leclanché cells, with a combined electromotive force of about 40 volts and an internal resistance of about 120 ohms. It furnished a current which remained practically constant for many hours, when enclosed in a circuit of 5000—10,000 ohms resistance. It also had the advantage of being always ready for use.

### 3. *Preparation of the Silver Solutions.*

The solutions of argentic nitrate were prepared from the crystallised salt. Those of the chlorate, perchlorate, ethyl-sulphonate, naphthalene-sulphonate, benzene-sulphonate, pseudo-cumene-sulphonate and acetate, were made by neutralising known amounts of these acids with moist argentic oxide, passing the solution through an asbestos filter, and diluting to a suitable volume. Argentic dithionate ($Ag_2S_2O_6$) was obtained by the reaction of exactly equivalent quantities of baric dithionate and argentic sulphate. To make argentic fluosilicate, a solution of hydrofluosilicic acid was saturated with argentic oxide; dilute baric hydrate solution was then added cautiously, until the brown color of argentic oxide commenced to appear in the precipitate of baric fluosilicate. The neutral solution was then filtered and diluted.

### 4. *Description of a Determination in Detail.*

The description of this determination, made with a solution of argentic nitrate which was about $\frac{1}{10}$ normal, will best illustrate our method of experiment and calculation. The electrolysis was

conducted at a temperature of 26°, and the solution thereupon divided into four portions, which are numbered in the following table in the order in which they were taken out; consequently, No. 1 represents the *lowest* stratum in the apparatus. Column I contains the weights of these portions; II, the amount of silver found in each; III, the amount each portion would have contained if no change had occurred, estimated from the fact that 1 gram of the solution originally contained 1.139 milligram of silver.

TABLE I.

| Portion. | I. | II. | III. | Diff. |
|---|---|---|---|---|
| 1 | 20.09 grams | 39.66 millig. | 22.88 millig. | + 16.78 millig. |
| 2 | 5.27 | 5.96 | 6.00 | — 0.04 |
| 3 | 5.33 | 6.04 | 6.07 | — 0.03 |
| 4 | 27.12 | 14.14 | 30.89 | — 16.75 |
| | 57.81 | 65.80 | | |

It will be seen that the strength of two middle portions has remained constant, within the errors of determination; we also find a close agreement in the second test, which demands that the mean concentration shall remain unchanged; the value 65.80/57.81 = 1.138, scarcely different from the original strength 1.139.

The measurement of the electrical current as described above informed us that a quantity of electricity equivalent to the precipitation of 32.10 mg. of silver had passed through the apparatus; while a silver-voltameter, placed in the circuit for our better assurance, contained 32.2 mg.; the former value was accepted as the more trustworthy.

Following Hittorf,[1] we based these calculations upon our data: The solution at the anode (1) received from the latter 32.1 mg. Ag, and the uppermost layer (4) gave up the same amount to the cathode. Owing to the changes in concentration, the values in the above table are not absolutely correct, since 1 gram of solution does not always contain the same weight of water, as had been provisionally assumed. But the necessary correction is small and readily made. Let $\nu$ be the ratio of the molecular weights of silver and the salt in question; in this special case $\nu = \frac{170}{108} = 1.57$. Let $a$ represent the amount of silver contained in 1 gram of

[1] Hittorf, Ann. Phys. Pogg. **98**, 19.

unaltered solution, being consequently dissolved in $(1 - av)$ grams of water. If, after electrolysis, $q$ grams of the solution about one electrode are found to contain $b$ grams of silver, the gain or loss will be represented by $\pm b - \frac{a(q - bv)}{1 - av} = \pm \frac{b - aq}{1 - av}$. As $b - aq$ is the value given in the column of differences, the factor $\frac{1}{1 - av}$ represents the necessary correction. Consequently, after completing the deficit of portion 4 by the addition of the small deficits in 2 and 3, we have for the *rate of transference of the negative ion*,

$\frac{16.78}{32.10} / .0017$ and $\frac{16.82}{32.10} / .0017$, or a mean value of 0.524.

As already stated, the determination was usually simplified by dividing the liquid into two portions instead of four.

In this experiment there was a second apparatus placed in series in the circuit; hence the mean intensity of the current was only 0.0012 ampère, and the electrolysis lasted seven hours. We frequently saved time and used our battery to better advantage by performing two simultaneous electrolyses in parallel circuits, each of which must, of course, contain its own resistance-box; by means of a properly constructed switch, we could apply the measuring circuit to either box at will, thus securing the measurement of both electrolyses with the same galvanometer and element. We may also state here that the last was frequently compared with another cell of the same construction and was always found to be exactly equivalent to it in electro-motive force, a proof that it did not vary during the course of our experiments.

### 5. *Rates of Transference of the Negative Ion.*

Hereafter $t$ implies the temperature during electrolysis; $m$ the molecular concentration (gram-molecules per liter); $f_1$ the milligrams of silver precipitated on the cathode according to galvanometric measurement; $f_2$ the same value according to the voltameter whenever it was used; $n$ the rate of transference.

*Argentic Nitrate.*

| | | | | |
|---|---|---|---|---|
| 1) $t = 20°$ | $m = 0.1043$ | $f_1 = 83.5$ | $f_2 = 83.6$ | $n = 0.528$ |
| 2) $t = 26°$ | $m = 0.0521$ | $f_1 = 76.7$ | | $n = 0.524$ |
| 3) $t = 26°$ | $m = 0.0250$ | $f_1 = 48.0$ | | $n = 0.5223$ |
| 4) $t = 0°$ | $m = 0.0250$ | $f_1 = 48.0$ | | $n = 0.5383$ |
| 5) $t = 26°$ | $m = 0.0105$ | $f_1 = 32.10$ | $f_2 = 32.2$ | $n = 0.524$ |
| 6) $t = 26°$ | $m = 0.0105$ | $f_1 = 32.10$ | $f_2 = 32.2$ | $n = 0.524$ |

In 3) and 4) and in 5) and 6) both pieces of apparatus were in the same circuit.

*Argentic Chlorate.*

| | | | | | |
|---|---|---|---|---|---|
| 1) | $t = 24.8°$ | $m = 0.0245$ | $f_1 = 39.88$ | $f_2 = 39.5$ | $n = 0.503$ |
| 2) | $t = 24.8°$ | $m = 0.0245$ | $f_1 = 51.72$ | | $n = 0.499$ |

*Argentic Perchlorate.*

| | | | | | |
|---|---|---|---|---|---|
| 1) | $t = 24.8°$ | $m = 0.0247$ | $f_1 = 39.88$ | $f_2 = 39.5$ | $n = 0.515$ |
| 2) | $t = 24.8°$ | $m = 0.0247$ | $f_1 = 51.72$ | | $n = 0.512$ |

In studying these two solutions, 1) and 1) and 2) and 2) were in the same circuits.

*Argentic Ethyl-sulphonate.*

| | | | | | |
|---|---|---|---|---|---|
| 1) | $t = 24.8°$ | $m = 0.0243$ | $f_1 = 58.30$ | | $n = 0.385$ |
| 2) | $t = 24.8°$ | $m = 0.0243$ | $f_1 = 48.47$ | $f_2 = 48.34$ | $n = 0.389$ |
| 3) | $t = 25°$ | $m = 0.00606$ | $f_1 = 18.10$ | | $n = 0.384$ |

*Argentic Benzene-sulphonate.*

| | | | | | |
|---|---|---|---|---|---|
| 1) | $t = 24.8°$ | $m = 0.0250$ | $f_1 = 48.47$ | $f_2 = 48.34$ | $n = 0.343$ |
| 2) | $t = 24.7°$ | $m = 0.0250$ | $f_1 = 17.85$ | | $n = 0.351$ |

2) of the former and 1) of the latter solution were electrolysed in series.

*Argentic Pseudocumene-sulphonate.*

| | | | | |
|---|---|---|---|---|
| 1) | $t = 24.2°$ | $m = 0.0235$ | $f_1 = 61.62$ | $n = 0.293$ |
| 2) | $t = 29.2°$ | $m = 0.02216$ | $f_1 = 38.24$ | $n = 0.2947$ |
| 3) | $t = 0°$ | $m = 0.02216$ | $f_1 = 38.24$ | $n = 0.2732$ |
| 4) | $t = 0°$ | $m = 0.02216$ | $f_1 = 42.79$ | $n = 0.2731$ |

2) and 3) were electrolysed in series.

*Argentic Naphthalene-sulphonate.*

| | | | | | |
|---|---|---|---|---|---|
| 1) | $t = 29.2°$ | $m = 0.01292$ | $f_1 = 33.95$ | | $n = 0.390$ |
| 2) | $t = 25.0°$ | $m = 0.0250$ | $f_1 = 39.75$ | $f_2 = 39.5$ | $n = 0.386$ |

*Argentic Acetate.*

In examining this salt, we were surprised to find that the middle layers of the solution did not remain unchanged, and that the mean concentration after electrolysis did not agree with the

original standard. This irregularity is probably due to the slight solubility of the salt, since it can easily happen that the solution about the anode becoming over-concentrated, some of the salt crystallises out and vitiates the result. In fact, we did succeed in obtaining reliable values when we had recourse to a highly dilute solution.

1) $t = 25°$ $m = 0.00972$ $f_1 = 20.80$ $n = 0.375$
2) $t = 24°$ $m = 0.00972$ $f_1 = 23.99$ $n = 0.377$

*Argentic Dithionate.*

1) $t = 24.8°$ $m = 0.0246$ $f_1 = 33.40$ $n = 0.604$
2) $t = 29.2°$ $m = 0.0246$ $f_1 = 46.70$ $n = 0.604$
3) $t = 0°$ $m = 0.0246$ $f_1 = 46.70$ $n = 0.605$
4) $t = 24.2°$ $m = 0.0246$ $f_1 = 48.85$ $n = 0.606$
5) $t = 0°$ $m = 0.0246$ $f_1 = 45.80$ $n = 0.603$

2) and 3) were electrolysed in series.

*Argentic Fluosilicate.*

1) $t = 22.2°$ $m = 0.02815$ $f_1 = 60.28$ $n = 0.647$
2) $t = 22.2°$ $m = 0.02815$ $f_1 = 37.44$ $n = 0.647$

In table II we summarise these values of $n$, with the corresponding temperatures and concentrations.

TABLE II.

| Argentic | $n$. | $t$. | $m$. |
|---|---|---|---|
| Nitrate, | 0.523 | 25° | 0.1 — 0.01 |
| | 0.539 | 0° | |
| Chlorate, | 0.505 | 25° | 0.0245 |
| Perchlorate, | 0.514 | 25° | 0.0247 |
| Ethylsulphonate, | 0.385 | 25° | 0.0243 — 0.0061 |
| Naphthalene-sulphonate, | 0.390 | 30° | 0.0250 — 0.013 |
| | 0.386 | 25° | |
| Pseudocumene-sulphonate, | 0.293 | 25° | 0.023 |
| | 0.273 | 0° | |
| Benzene-sulphonate, | 0.347 | 25° | 0.025 |
| Acetate, | 0.376 | 25° | 0.097 |
| Dithionate, | 0.604 | 25° | 0.0246 |
| | 0.604 | 0° | |
| Fluosilicate, | 0.466 | 22° | 0.0282 |

Argentic nitrate has been carefully studied by Hittorf,[1] who found that between the concentrations 0.3 and 0.024 the rate of transference does not vary, the mean value being 0.526 at 19°. We came to the same conclusions for variations of concentration

[1] Ann. Phys. Pogg. **89**, 199.

from 0.1 to 0.01, and we found a value which, when reduced to the same temperature, very nearly agreed with his, 0.527 at 19°. The acetate result given above also agrees well with Hittorf's (0.373 where $t = 15°$ and $m = 0.05$).

### 6. *Conducting Power of the Silver Salts and its Relation to the Rate of Transference.*

It will be noted that the rate of transference is a value varying with the compound, since it merely expresses the share of the one ion in the total movement. If $u$ is the actual velocity of the positive ion and $v$ that of the anion, $n = \frac{v}{u+v}$; and the rate of the positive ion, $1 - n = \frac{u}{u+v}$. Kohlrausch,[1] as is well known, has propounded the simple hypothesis that the conducting power of a molecule of an electrolyte is represented by the sum of the velocities of its ions,

$$\lambda = u + v.$$

His experiments, however, did not seem to give the requisite support to this theory, some salts giving approximate results, but those of weak bases and acids giving utterly discordant figures. The difficulty is removed if we assume that the conduction is not performed by all the molecules of the electrolyte, but only by those whose ions are actually in independent motion. This is Arrhenius' principle of conductive activity.[2] Kohlrausch's values for molecular conductivity are a function of the total number of molecules of the electrolyte between the electrodes; according to Arrhenius, the coefficient of activity, *i. e.* the proportion of molecules actually engaged in conduction, not only varies for different compounds, but also increases for any one compound with its dilution, and approaches unity for extreme dilutions. It is only in this limiting case that Kohlrausch's equation becomes absolutely true; this is the view that Kohlrausch himself had expressed with regard to his law, whose accuracy, he said, could only be tested by experiments with highly dilute solutions. Ostwald's examination of the conducting power of highly attenuated solutions of a very large number of electrolytes[3] has afforded very valuable support to these recent views.

Since, however, the quantities $u$ and $v$ are so closely connected

[1] Fr. Kohlrausch, Ann. Phys. Wied. **6**, 1.
[2] S. Arrhenius, Sur la conductibilité, etc., Stockholm, 1884.
[3] Ztschr. phys. Chem. **1**, 61 and 97.

with the rate of transference of the ions, a study of the latter in dilute solutions must afford powerful means of testing the truth of Kohlrausch's law with Arrhenius' emendations. This was the chief motive of our work, and we must now, therefore, proceed to compare the values which we have given in §5 with the conducting power of the same salts. Accordingly, the necessary measurements of conduction were made by one of us (W. N.), by Kohlrausch's method, which with various valuable modifications has been described by Prof. Ostwald.[1] The values which we present are scaled upon the conducting power of mercury as unity, and the calculations are based upon Kohlrausch's determination of the molecular conductivity of argentic nitrate.[2]

The following table gives the conducting power of the different silver salts. The molecular concentration (gram-molecules in the liter) $m$, was calculated from the percentage composition as found by analysis, and the specific gravity determined at 18°, although this barely differed from that of water. There was no appreciable contraction when additional water was added for dilution; but a proper correction was made for the conduction by the water itself, which was found to be $2.5 \times 10^{-10}$.

TABLE III.

| $m$. | $\lambda \times 10^8$ at 25°. | | | | |
|---|---|---|---|---|---|
| | $AgNO_3$. | $AgClO_3$. | $AgClO_4$. | $Ag(C_2H_5SO_4)$. | $Ag(C_6H_5SO_3)$. |
| 0.025 | 1126 | 1045 | 1109 | ... | ... |
| 0.015 | 1153 | 1103 | 1139 | ... | 846 |
| 0.007 | 1188 | 1123 | 1160 | 905 | 874 |
| 0.003 | 1206 | 1151 | 1182 | 930 | 897 |
| 0.0015 | 1221 | 1160 | 1194 | 943 | 900 |
| 0.0008 | 1232 | 1163 | 1200 | 949 | 906 |

| $m$. | $\lambda \times 10^8$ at 25°. | | | | |
|---|---|---|---|---|---|
| | $Ag(C_6H_{11}SO_3)$. | $Ag(C_{10}H_7SO_3)$. | $AgC_2H_3O_2$. | $\frac{1}{2}Ag_2S_2O_4$. | $\frac{1}{2}Ag_2SiFl_6$. |
| 0.025 | 734 | ... | ... | 1253 | 995 |
| 0.015 | 762 | 882 | ... | 1343 | 1020 |
| 0.007 | 791 | 893 | 897 | 1383 | 1054 |
| 0.003 | 813 | 926 | 926 | 1442 | 1081 |
| 0.0015 | 826 | 941 | 944 | 1474 | 1096 |
| 0.0008 | 836 | 951 | 949 | 1505 | 1100 |

[1] Ibid. **2**, 563.

[2] As Kohlrausch worked at 18°, while the present determinations were made at 25°, the coefficients of temperature were determined by special experiments for various dilutions of $AgNO_3$. For the details of these results we must refer to the German version of our paper.

Ostwald has found[1] that the sodium salts of numerous monobasic acids have almost identically progressing coefficients of activity; the same regularity may be observed in the present series. The ratios of the conductivity of a salt in various states of dilution agree, for the silver salts of the monobasic acids, within limits that scarcely transcend the probable errors of observation. We shall utilise this fact in finding the limit of the conductivity for extreme dilution; for, at the concentration 0.0008, the dissociation of the molecules is not yet complete, although very nearly so. If we remember that, according to Kohlrausch's measurements, when $m = 0.0008$, $\frac{1069}{1077}$ of the molecules of argentic nitrate are dissociated, we can fairly assume that the limiting values of $\lambda$ for the other silver salts may be obtained by raising by 0.75 per cent. the values found for $m = 0.0008$.

Table IV summarises the measurements made to determine the effect of temperature upon conducting power; in these the platinum electrodes usually employed were replaced by silver ones, which gave very sharp readings. The measured conductivities at 0°, 18° and 28° are denoted by $\lambda_0$, $\lambda_{18}$ and $\lambda_{28}$ respectively; to obtain the coefficient of temperature $\frac{\lambda_{28}}{\lambda_{18}}$ must be diminished by 1 and divided by 10: $\frac{\lambda_0}{\lambda_{25}}$ was calculated from such an interpolated value of $\lambda_{25}$.

TABLE IV.

| | $m$. | $\frac{\lambda_0}{\lambda_{18}}$ | $\frac{\lambda_{28}}{\lambda_{18}}$ | $\frac{\lambda_0}{\lambda_{25}}$ |
|---|---|---|---|---|
| $AgNO_3$, . . . . | 0.1 | 0.638 | 1.213 | 0.555 |
| | 0.02 | 0.638 | 1.217 | 0.554 |
| | 0.005 | 0.632 | 1.222 | 0.548 |
| $AgClO_3$, . . . . | 0.005 | 0.626 | 1.222 | 0.542 |
| $AgClO_4$, . . . . | 0.005 | 0.632 | 1.224 | 0.547 |
| $AgC_7H_7SO_3$, . . | 0.005 | 0.615 | 1.242 | 0.526 |
| $AgC_6H_5SO_3$, . . . | 0.005 | 0.607 | 1.241 | 0.519 |
| $AgC_2H_3O_2$, . . . | 0.005 | 0.611 | 1.237 | 0.524 |
| $AgC_9H_{11}SO_3$, . . | 0.025 | 0.609 | 1.242 | 0.521 |
| | 0.006 | 0.606 | 1.246 | 0.517 |
| $\frac{1}{2}Ag_2S_2O_6$, . . . | 0.025 | 0.631 | 1.222 | 0.547 |
| | 0.006 | 0.631 | 1.226 | 0.544 |

[1] Ostwald, Ztschr. phys. Chem. **2**, 847.

### 7. *Test of the Law of Kohlrausch for Extreme Dilutions.*

For this purpose we need, besides the limiting values for conduction, which we have just shown to be attainable, the limiting values for the rate of transference, likewise for extreme dilution.

At the close of section 5 we noted that Hittorf found the value of $n$ to be independent of the state of dilution where $m < 0.3$ in the case of $AgNO_3$, and that we confirmed his result by our own experiments on this and other salts. Consequently the values found for this rate, whenever $m = 0.025 - 0.01$, can be assumed to hold good for infinite dilutions. The reason becomes apparent when, considering the inactive molecules as stationary, we remember that a molecular concentration 0.01 means a proportion of one silver ion to 5550 molecules of $H_2O$. The resistance which such an ion would encounter cannot differ from that of pure water.

The testing of Kohlrausch's law can now be readily accomplished by multiplying the limiting value of conductivity into $(1 - n)$, the rate of transference of the positive ion; the product, which represents the molecular velocity of the silver ion, must remain constant for all the monobasic salts.

TABLE V.

| | $\lambda \times 10^6$. | $(1 - n)$. | $\lambda (1 - n)\, 10^6$. |
|---|---|---|---|
| $AgNO_3$, . . . . . | 1242 | 0.477 | 592 |
| $AgClO_3$, . . . . . | 1172 | 0.499 | 585 |
| $AgClO_4$, . . . . . | 1208 | 0.486 | 587 |
| $AgC_7H_7SO_4$, . . . . | 956 | 0.615 | 588 |
| $AgC_{14}H_{13}SO_3$, . . . | 958 | 0.614 | 588 |
| $AgC_6H_5SO_3$, . . . . | 913 | 0.653 | 596 |
| $AgC_9H_{11}SO_3$, . . . | 842 | 0.707 | 595 |
| $AgC_2H_3O_2$, . . . . . | 956 | 0.624 | 597 |

The velocity of Ag as found in these salts proves to be nearly constant: the deviations from the average $591 \times 10^{-8}$ are within the limits of the probable errors of observation, especially as the latter have a cumulative effect. We consider this an additional confirmation of the recent electrolytic hypotheses.

This average, which applies for 25°, may be considered the true value for the velocity of the Ag ion, within a few thousandths, provided Kohlrausch's determination of the limit of conduction for argentic nitrate contains no important error. We can now calculate the ion's velocity at 0°, from the values of $n$ at that temperature for argentic nitrate and pseudo-cumol-sulphonate (table II), and

the values of $\lambda$ reduced from table III by the ratio $\frac{\lambda_0}{\lambda_{25}}$ (table IV).

$$1242 \times 0.461 \times 0.548 = 314$$
$$842 \times 0.727 \times 0.517 = 317 \quad \text{Mean} = 315.5.$$

We again call attention to the smallness of the deviation. Now, since $\lambda = u + v$, we can obtain the velocities of all our negative ions, by subtracting the velocity of the silver from the respective conducting powers. In table VI we find on the first line the velocities at 25°; on the second, those at 0°; on the third, the coefficient of temperature between 25° and 0°, as calculated from the formula $v = v_{25}\,[1 + \alpha\,(t - 25)]$, $\alpha$ being the coefficient: all the values must be multiplied by the factor given in the final column.

TABLE VI.

| | $C_9H_{11}SO_3$. | $C_6H_5SO_3$. | $C_2H_3O_2$. | $C_2H_5SO_4$. | |
|---|---|---|---|---|---|
| I | 248 | 318 | 361 | 368 | $\times 10^{-5}$ |
| II | 118 | 156 | 183 | ... | $\times 10^{-5}$ |
| III | 210 | 203 | 197 | ... | $\times 10^{-4}$ |

| | $C_{10}H_7SO_3$. | $ClO_3$. | Ag. | $ClO_4$. | $NO_3$. | |
|---|---|---|---|---|---|---|
| I | 369 | 587 | 591 | 621 | 640 | $\times 10^{-5}$ |
| II | 180 | 322 | 316 | 347 | 364 | $\times 10^{-5}$ |
| III | 198 | 181 | 186 | 177 | 175 | $\times 10^{-4}$ |

The close agreement of the velocities shown in line I with the observations of the rates of transfer and of the conduction, is proved by the fact that the calculated and observed values agree within ½ per cent. in all cases. A glance at table VI, in which the velocities are arranged according to magnitude, will bring out a striking relation of the coefficients of temperature. *The coefficient of temperature decreases when the velocity increases.* We may add that the coefficients of temperature for the monovalent ions OH and H, which have an exceptionally great velocity, can be added to this series.[1]

| | OH. | H. | |
|---|---|---|---|
| I | 187 | 350 | $\times 10^{-7}$ |
| III | 159 | 137 | $\times 10^{-4}$ |

A result of this regularity would be that, as the temperature rises, the rates of transference would all approach the value 0.5, and the conducting powers $\lambda_\infty$ of all salts would approach equality.[2]

If we attempt to calculate the velocity of the silver ion from

[1] Nernst, Ztschr. phys. Chem. **2**, 626.

[2] Cf. Arrhenius, l. c. p. 45.

the salts of the two dibasic acids which we have studied, we obtain from

$$Ag_2S_2O_6: 1540 \times 0.394 = 0.607$$
$$Ag_2SiF_6: 1120 \times 0.534 = 0.598$$

These values are somewhat greater than those found before. To avoid a conflict with the necessary assumption that the free ion of silver must have the same velocity, no matter whether it has been liberated from a mono- or dibasic acid ion, we must admit that the rates of transfer in these two salts, which were measured at a concentration 0.025 and 0.028 respectively, must change on further dilution. As our investigation was brought to a close by the departure of one of us from Leipsic, we were unable to set this question at rest; we note in passing, however, that the dissociation hypothesis makes it probable that the compounds of multivalent radicals are still undergoing changes at dilutions in which monobasic compounds show a constant rate of transference. The dissociation products for $Ag_2S_2O_6$, for instance, are Ag, $AgS_2O_6$ and $S_2O_6$; consequently in such dilutions as 0.025 there may exist, besides the ions $+Ag$, $+Ag$, $-S_2O_6$, upon which we based our calculations, a considerable set of ions $+Ag$, $-AgS_2O_6$; if these decompose on further dilution, the rate of transference must continue to change. We have here considerations similar to those which Hittorf used so skilfully nearly thirty years ago,[1] in obviating the difficulties which the abnormal behavior of cadmic iodide threatened to cast in the way of his theory.

PHYSICO-CHEMICAL LABORATORY, LEIPSIC. NEWPORT, R. I.

## DECOMPOSITION OF COBALT AND NICKEL.[2]

BY GERHARD KRÜSS AND F. W. SCHMIDT.

We have been engaged in a redetermination of the atomic weights of cobalt and nickel, employing the method first devised by Clemens Winkler, of decomposing gold chloride solution by weighed amounts of cobalt or of nickel, and weighing the pre-

[1] Hittorf, Ann. Phys. Pogg. **106**, 546 (1859).

[2] Abstract of an article in Ber. d. chem. Ges. **22**, 11; prepared by E. Renouf.

cipitated gold, thus obtaining the equivalents of cobalt or nickel in terms of gold. As Krüss recently redetermined with great accuracy the atomic weight of gold, this method promised better results than when it was first employed by Winkler twenty years ago, and we hoped to confirm in this way the figures found by Clemens Zimmermann in his determination—cobalt 58.74, nickel 58.56.

Despite numerous attempts, we neither succeeded in obtaining Zimmermann's figures, nor in confirming the atomic weights formerly found by Winkler by the same method. We first found that it is impossible to precipitate quantitatively by nickel or cobalt from a neutral gold chloride solution an equivalent amount of gold, because in consequence of polarisation the precipitated gold attacks the nickel or cobalt chloride solution which has been formed, reversing the original reaction and reprecipitating minute quantities of cobalt or nickel which remain undissolved mixed with the gold. To determine how much metal had taken part in this secondary reaction, the precipitated gold was washed, dried, ignited, and weighed, then dissolved in *aqua regia*, and after evaporating all free acid, reprecipitated by sulphurous acid, and weighed. There was a noticeable loss of weight between the two weighings, and the difference was deducted from the weight of the metallic nickel or cobalt first taken.

Despite these precautions, such varying figures were obtained that the variations were evidently due to some other cause than ordinary analytical errors. In washing the gold which had been reprecipitated by sulphurous acid, the filtrate had a red color, due to cobalt chloride. We noticed that the wash-water dripping from the filter gradually lost this red color and became tinged with a greenish hue, so slight that it had before escaped observation. This part of the wash-water was evaporated in a platinum dish and left a slight residue, which dissolved with green color in concentrated hydrochloric acid on heating; when the solution cooled it became nearly colorless.

The same reactions occurred in an atomic weight determination of nickel, on washing the gold reprecipitated by sulphurous acid; by evaporating the wash-waters and dissolving in hydrochloric acid, a solution was obtained differing in its reactions from the chlorides of any known element.

The amount of chloride obtained in this way was very small. An attempt was made to obtain more by extracting nickel sulphide with yellow ammonium sulphide, and repeating this treatment for

weeks; a residue was finally obtained quite insoluble in ammonium sulphide, which contained a much greater percentage of the new substance than the original nickel salt.

Various other methods were tried, till finally the observation that the new oxide, fused with alkaline hydroxides, dissolves in the fused mass, while cobalt and nickel oxide remain undissolved, pointed out the way to obtain the new oxide pure and in sufficient amount from either nickel or cobalt salts. From 50 grams of nickel oxide we obtained 1 gram pure new oxide.

Following are some of the characteristic reactions of the new element: The acidulated chloride solution is not precipitated by sulphuretted hydrogen; ammonium sulphide precipitates from the neutral solution a black sulphide; ammonia forms a very voluminous white precipitate resembling zinc hydroxide, insoluble in excess of ammonia; potassium hyroxide ($\frac{1}{2}$ normal solution) also precipitates white hydroxide quite insoluble in even a large excess of potassium hydroxide. This is a sharp distinction from aluminium hydroxide, no traces of which could be found in the new oxide. Ignited with cobalt solution, it does not yield Thenard's blue, but turns pale brown. When the oxide has been ignited for some time over the blast-lamp, it forms a soft white powder which dissolves readily in cold dilute hydrochloric acid. The strongly acid chloride solution shows the peculiar greenish yellow shimmer which first arrested our attention. When quite anhydrous and free from acid, the chloride is white and forms a colorless solution in water; but if hydrochloric acid vapor is blown over the chloride it turns greenish, and its solution in water is colored. When heated in a current of hydrogen the acid does not resemble nickel or cobalt oxides, for its weight remains unchanged even when submitted to violent ignition in an atmosphere of hydrogen. We have succeeded, however, in isolating the metal from which the white oxide is derived by electrolysis of an aqueous solution of the chloride. The metal was also obtained by drying the chloride in an atmosphere of carbon dioxide, and reducing it by hydrogen at red heat. The metal is black, in thin scales brownish black; if isolated by electrolysis, it is easily soluble in acids, but is soluble with difficulty after being heated to a high temperature in hydrogen.

Further communications will soon follow, and we now purposely refrain from all speculation regarding the atomic weight of cobalt, nickel, or the new metal, but we wish to reserve this field of work for the present.

# REVIEWS AND REPORTS.

## Recent Progress in Industrial Chemistry.

In a review of the most important directions in which chemical industries have been extended and developed during a given period, the aim should be to present a correct outline of those improvements in processes which have proved successful in actual practice. A list of patents and suggestions is of little interest, for but few of these ever come to actual trial on a large scale, and fewer still prove to be of permanent value. In the following pages the author has endeavored to follow the example of the able reports written for this journal ten years ago by Professor Mallet,[1] and to give prominence to the most important changes in industrial processes which have taken place since the above papers appeared.

### 1. Sulphuric Acid.

*Materials of Sulphuric Acid Manufacture.*—The first sulphuric acid manufactured was "fuming" acid, which was obtained in Bohemia by distilling ferric sulphate. The manufacture from sulphur was introduced in England in 1740. After that time sulphur was generally used until about 1833, when Perret & Sons, of Chessy, near Lyons, began to utilise in sulphuric acid-making the sulphur dioxide given off in the burning of copper ores. The monopoly of the exportation of Sicilian sulphur, granted in 1838 to a firm in Marseilles, though of brief duration, caused a general search for other sources of sulphur. Deposits of pyrites were developed in Westphalia, Hungary, France, Belgium, Ireland, and other countries, which supplied the wants of Europe for a long period. The pyrites from these sources has now been almost entirely supplanted by the cupreous pyrites of Spain and Portugal, which is burned chiefly for the copper and silver which it contains, with the production of sulphuric acid as a by-product. The use of sulphur for acid-making has been almost wholly abandoned in Europe. In 1887 there were imported into England 597,595 tons of pyrites, and only 32,624 tons of sulphur.

In the United States important deposits of pyrites occur, chiefly in New Hampshire, Massachusetts, and Virginia; the total quantity produced from these sources amounted in 1887 to 53,233 tons. During the same year there were imported from Canada about 35,000 tons, and from Spain 16,600 tons. The importation of sulphur from Sicily amounted in 1887 to 88,593 long tons. As

[1] Mallet, The Progress of Industrial Chemistry. This Journal **9** and **10**.

these figures show, sulphur is still more generally used than pyrites in the United States for the manufacture of sulphuric acid. It was estimated[1] that in 1884 306,000 tons of acid were made from sulphur and 122,000 tons from pyrites. In 1887 only four additional works had taken up the use of pyrites. The reason of this delay in the introduction of pyrites on the part of American manufacturers is probably the great demand for sulphuric acid in this country for the manufacture of fertilizers and the refining of petroleum; the price of acid is therefore comparatively high, and the practice of rigid economy unnecessary. The introduction of pyrites has also to contend against the higher cost and more complicated working of the apparatus which its use involves. Another advantage of sulphur is that it produces acid free from arsenic, an important consideration if the acid is to be used in the manufacture of chemicals used in the preparation of food or medicines, though of no consequence in the petroleum or fertilizer industries. Further, when sulphur is used, the burner gases are somewhat richer than those from pyrites, since in the latter case a portion of the oxygen of the air admitted remains behind in the oxide of iron of the cinders. Lunge[2] calculates that one kilogram of free sulphur gives 6109 liters of gas, while the same weight of sulphur in the form of pyrites gives 8145 liters. This renders it necessary to provide one-fourth to one-third more chamber space for pyrites than for sulphur. There can, however, be no question that pyrites is decidedly the cheaper material, especially when the cinders are worked for copper. Dr. Francis Wyatt, in his valuable review of the development of American chemical industry,[3] estimates that by the manufacture of acid at the pyrites mines the cost might be reduced from $5.50 to $4.20 per ton of chamber acid. To compete with this, brimstone must be sold at $14 per ton, whereas the price in 1887 ranged from $19 to $24.

Generally speaking, works near Philadelphia and in the South are still using sulphur, while in the more complete and modern plants in the neighborhood of New York and in New England pyrites is employed.

*Extraction of Sulphur.*—The methods of extracting sulphur from the gangue in Sicily have been greatly improved in recent years by the introduction of larger kilns for burning the ore. According to Consul Carroll,[4] these have in some cases the capacity of 5000 tons each, and the smelting operation requires several months for its completion. In these kilns from two-fifths to three-fifths of the sulphur contained in the ore is obtained, or from two to three times as large a proportion as in the small kilns formerly used. More perfect methods of extraction are employed in Sicily to some extent, but owing to the scarcity of fuel, costliness of

[1] Mineral Resources of the United States, 1883–4.
[2] Sulphuric Acid and Alkali, Vol. I, p. 240.
[3] Engineering and Mining Journal, 1887, and Mineral Resources, 1886, p. 671.
[4] U. S. Consular Reports, No. 92, 1888, p. 182.

machinery, and lack of intelligent labor, the greater part of the sulphur is still obtained by means of the "calcaroni" or large kilns. According to Vincent,[1] the process of Tour and Debreuil has been introduced into Sicily. This consists in immersing the ore, contained in iron baskets, in a solution of calcium chloride heated to 130° C., or above the melting point of sulphur. By this process it is possible to extract all but four or five per cent. of the sulphur contained in the ore. Consul Carroll states that Durand's process of fusion in iron pots and ladling out the melted sulphur, Hirzel's furnace, Thomas's process of fusion by superheated steam, and Bollmann's method of extraction by carbon disulphide, are also to some extent used.

In the United States sulphur is obtained on a commercial scale only at Cove Creek, Utah. The deposits are stated to be very extensive, and the production of sulphur has rapidly increased during the past few years. In 1887 the amount obtained was about 3000 tons. The sulphur is extracted by fusion with superheated steam. Cedar wood for fuel is abundant and cheap.

*Pyrites Burners.*—The furnaces used for burning pyrites have been often described, and no important changes have been lately introduced. The forms generally used in Europe and this country are grate-burners for lump ore, and shelf-burners for "smalls." The "Spence Mechanical Furnace," now largely used in Europe and at some works in this country, is a shelf-burner for small ore in which the charge is pushed from one shelf to another by steam-power instead of by hand.

*Utilisation of Pyrites Residue.*—With modern burners for smalls, and especially with the Spence furnace, it is possible to burn the pyrites down to one per cent. of sulphur. The resulting cinders from non-cupreous pyrites consist chiefly of ferric oxide, and are almost absolutely free from phosphorus. Such cinders are valuable as iron ore. According to Dr. Wyatt, several acid works near New York are now selling their non-cupreous pyrites cinders to iron-smelters at three or four dollars per ton.

Cinders from pyrites containing notable quantities of copper are treated by the wet extraction process. If much silica and little silver are present, as in the case of cinders from most kinds of American pyrites, it is found best to smelt the cinders with the addition of raw pyrites in the form of "fines," and thus to obtain a "matte" containing 50 to 60 per cent. of copper. By this method, however, the iron and silver contained in the cinders are lost. If, on the other hand, there are present two or three ounces per ton of silver and but little silica, as is generally the case with the cinders from Spanish ores, the Henderson wet process is used for the extraction of copper and silver.

It is stated that 400,000 tons of pyrites residue are annually treated by this process in England alone. The cinders are roasted

[1] Trans. by Bayley, this Journal **6**, 63.

with salt, sometimes with the addition of the mattes obtained by smelting siliceous ores. The cinders contain copper chiefly in the form of sulphate and sulphide. After the roasting with salt the copper is principally in the form of chloride, with a considerable proportion of oxide. Hydrochloric acid is given off during the roasting, and is condensed in the usual way. The resulting cinders are lixiviated, first with water, then with the dilute acid obtained in the operation. In the solution the silver is precipitated by potassium iodide or hydrogen sulphide, and the copper by scrap iron. This process is worked to some extent in this country, using the residues from Spanish pyrites, at Elizabeth, N. J., Natrona, Pa., and probably at other places.

*Modern Acid Works.*—The use of the Glover Tower has become general in Europe, but has not been taken up by more than one-half the works in this country. Near New York and in New England, however, are located several new works at which highly concentrated acid for use in refining petroleum and in making nitro-glycerin is made. These establishments are generally equipped with all the best appliances, such as shelf-burners for smalls, Glover and Gay-Lussac towers, and platinum concentrating apparatus, and are as complete and perfect as any works in Europe.

*Concentration of Sulphuric Acid.*—The chamber acid has generally a strength not above 50° B., corresponding to about 62 per cent. of $H_2SO_4$. This is strong enough for the manufacture of superphosphates, ammonium sulphate, and even for the salt-cake process. For the refining of petroleum, the manufacture of nitric acid, and especially in making nitro-compounds, acid of greater strength is needed. Acid from the Glover tower may reach a strength of 62° B., corresponding to 81.7 per cent. of $H_2SO_4$. Beyond this point the concentration must be carried on in platinum stills or glass retorts. Acid from the Glover tower cannot generally be concentrated in platinum, since it contains a large amount of ferric sulphate, which would deposit on the pan and do serious damage. When platinum stills are used, therefore, acid from the chambers is first concentrated in lead pans by the waste heat of the platinum stills or burners to 60° B., then run into the stills. In this country these are generally on the Faure and Kessler system, and consist of a pan of platinum, surmounted by a leaden dome cooled by a water-jacket. The great drawback to the use of platinum is its rapid corrosion, which is especially marked in the case of acid containing nitrogen compounds or considerable quantities of arsenic. Acid made from sulphur is free from arsenic, and that made from American pyrites is practically so. The oxides of nitrogen must be completely removed before distillation in platinum is attempted. This is done by the addition of a little ammonium sulphate, which decomposes the nitrogen compounds, forming water and free nitrogen.

According to W. H. Adams,[1] platinum stills would last almost indefinitely for the concentration of acid free from arsenic up to a strength of 65° B., or about 90 per cent. $H_2SO_4$. Such acid is strong enough for almost all purposes, but for the manufacture of nitro-benzene, nitro-glycerin, etc., further concentration is necessary. Beyond this point lead, iron and other substances are rapidly precipitated and adhere to the bottom of the pan, causing its speedy destruction, and it is in the removal of the last portions of water that the chief injury to the apparatus takes place. Within the last few years cast-iron retorts have been successfully used for the final concentration, and are now employed on a large scale in extensive works near New York. It is found that acid of 65° B. does not attack the stills, and no injury appears to result from the deposition of arsenic or other substances. The concentration is carried as far as possible in platinum; the acid is then run into the cast-iron stills and concentrated to 98 per cent. $H_2SO_4$. It is stated by Mr. Adams that a set of iron stills such as he describes is in use near New York in connection with platinum, and is producing 30,000 pounds per day of 98 per cent. acid.

In England the use of glass seems to be increasing, owing to the cheapness and perfection of the large retorts which are now made. By the use of glass, acid from the Glover tower may be concentrated directly, and no injury results from the presence of arsenic or nitrogen compounds. The final concentration, however, presents many difficulties, owing to the violent ebullition of the strong acid and the separation of sediments. The loss by breakage is therefore still very great.

SPENCER B. NEWBURY.

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### Determination of Carbon Monoxide in Gas-Mixtures.

The determination of carbon monoxide in gas-mixtures is usually effected by absorption in an ammoniacal[3] or a hydrochloric acid[3] solution of cuprous chloride. But it has been observed[4] that the volume of certain gases which contain but little monoxide is often increased, instead of diminished, by agitation with solutions of cuprous chloride. This increase of volume Hempel[5] ascribed to a failure on the part of the operator to remove the heavy hydrocarbons by strong sulphuric acid, before proceeding to a determination of the carbon monoxide. It was assumed that the solution of cuprous chloride, having absorbed heavy hydrocarbons which should have been taken out by sulphuric acid, was forced to give them, or a part of them, up again when agitated with a new portion

[1] Twenty Years' Progress in the Concentration of Sulphuric Acid; Proc. of Amer. Inst. of Mining Engineers, 1887.
[3] Hempel's Neue Methoden zur Analyse der Gase, p. 40.
[3] Winkler's Anleitung zur Untersuchung der Industriegase **1**, 38.
[4] Ber. d. chem. Ges. **20**, 2344.
[5] Ber. d. chem. Ges. **20**, 2344.

of gas in which the carbon monoxide was to be determined, and thus it might happen that a gas containing but little carbon monoxide would increase in volume when treated for its removal. This explanation was declared by Drehschmidt[1] to be insufficient and even erroneous, since the increase in volume referred to is often observed even after the removal of the heavy hydrocarbons by sulphuric acid. It is then suggested that the expansion is due to the feeble union of the carbon monoxide and cuprous chloride; in other words, that a solution of cuprous chloride containing carbon monoxide may give up a portion of the latter to any gas with which it is agitated. Moreover, it was found in every case of such increase of volume, that the presence of carbon monoxide in the gas could be established by combustion with palladium asbestus or by explosion.

It was also found that the absorption of carbon monoxide by cuprous chloride is rarely complete; never so, in fact, except when perfectly fresh solutions are employed; and that the amount which remains unabsorbed depends upon the quantity of carbon monoxide previously absorbed by the cuprous chloride, and upon the volume of the non-absorbable gas. It appeared also that the quantity remaining unabsorbed is greater when the hydrochloric acid solution is used, and that for this reason the ammoniacal solution is to be preferred. If the gas is allowed to stand over the liquid, the quantity of carbon monoxide in the gas diminishes with time in the case of the ammoniacal, but not in the case of the acid solution. The author explains this by the fact that carbon monoxide slowly precipitates metallic copper from ammoniacal cuprous solutions. He recommends that the gas, from which most of the carbon monoxide has been removed, be again agitated with a fresh solution of cuprous chloride, or that it be mixed with air and passed over heated palladium asbestus.

Hempel[2] admits that a solution of cuprous chloride may, under certain circumstances, give off gas, but he believes it to be improbable that a solution which is easily capable of absorbing four times its own volume of the gas should, when only partially saturated, give up carbon monoxide to another gas which is only slightly soluble in it. He therefore endeavors to find in the conduct of the gases, which are only mechanically absorbed by the solution, an explanation of the increase of volume. He says, in effect, that when, as in the experiments of Drehschmidt, the copper solution is treated (1) with a mixture of carbon monoxide and nitrogen, (2) with hydrogen and then (3) with a mixture of carbon monoxide and nitrogen, and (4) with nitrogen, it will first absorb nitrogen (1), which will for the most part be again given up when the solution is treated with hydrogen, and that the last will be in turn displaced by nitrogen (3 and 4). These facts, he says, explain without any difficulty the observations of Drehschmidt. He wholly

[1] Ber. d. chem. Ges. **20**, 2752. [2] Ibid. **21**, 898.

ignores the evident fact that whether in the case given there will be expansion or contraction, or no change in volume, will depend upon the relative solubility of nitrogen and hydrogen; and that, if there is expansion when the nitrogen is displaced by hydrogen, there must be contraction when the hydrogen is in turn displaced by nitrogen.

He remarks very justly that it is not permissible to employ the same absorbing liquids for the analysis of gases of widely differing composition; but that the errors which would be thus introduced may be obviated by repeating the analysis with a fresh portion of the gas. For a like reason, analyses made with entirely fresh absorbing liquids are not correct, and must be repeated. Drehschmidt,[1] in order to test the correctness of Hempel's explanation, treated solutions of cuprous chloride containing carbon monoxide with pure nitrogen. In each case an increase of volume was observed; and that this increase was due to carbon monoxide derived from the solution was proved by mixing the gas with oxygen and exploding, or by burning by means of palladium asbestus, and absorbing the carbon dioxide. He concludes that, in order to obtain sufficiently correct results with Hempel's apparatus, it is necessary to employ two absorption pipettes for the determination of carbon monoxide, one of which shall always contain a comparatively fresh solution of the cuprous chloride. Otherwise, the gas is to be mingled with air and the mixture passed over heated palladium asbestus.

H. N. Morse.

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### The Origin of Petroleum.

An interesting contribution to the evidence of the animal origin of petroleum has recently been made by C. Engler.[2] There are two theories concerning the origin of petroleum; the first, the so-called emanation theory, assumes petroleum to be generated by chemical decomposition of inorganic matter, in the heated interior of the earth; according to the second theory, petroleum is formed by the decomposition of vegetable or animal matter. Several hypotheses have been suggested by different chemists in support of the emanation theory, the most prominent being that of Mendelejeff, who thinks that water penetrating through crevices comes in contact with highly heated carburets of iron and other metals in the earth's pyrosphere, forming metallic oxides and gaseous hydrocarbons, which condense to petroleum in the cooler portions of the earth's crust. While it is true that Mendelejeff and other chemists before him have succeeded in obtaining mixtures of hydrocarbons resembling petroleum, by reactions in the laboratory similar to those supposed, the weight of geologi-

[1] Ber. d. chem. Ges. **21**, 2158.

[2] Ber. d. chem. Gesell. **21**, 1816.

cal and paleontological evidence is against all theories which assume an inorganic source of petroleum, and points to marine animal life as the probable source.

Recently Krämer and Böttger,[1] in a study of the hydrocarbons contained in crude petroleum, advanced the opinion that certain of these hydrocarbons must have been formed by distillation of organic matter at comparatively low temperature and high pressure. Engler had at this time opportunity to use an apparatus designed for factory work, in which he could distill large quantities of liquid under a pressure of two atmospheres. Influenced by Krämer's suggestion, he distilled 1000 lbs of menhaden oil at a temperature of 350°–400° and a pressure of two atmospheres. The distillate consisted of combustible gases, water, and 600 lbs of oil resembling crude petroleum in appearance and reactions. Of this oil 26 per cent. boiled below 150°, 58 per cent. between 150° and 300°, 16 per cent. above 300°. The two higher boiling portions have not yet been examined. By fractional distillation of the portion boiling below 150°, Engler has thus far isolated pentane, hexane, heptane, octane and nonane of the paraffin series, and finds that hydrocarbons of the secondary series are also present; in short, this oil seems identical with that portion of crude petroleum boiling below 150°. As fish oil is a mixture of triglycerides, chiefly of oleïc and stearic acids, Engler thought it of interest to distill chemically pure triglycerides of these acids, and the free acids under pressure. As apparatus he used thick glass tubes bent at an obtuse angle, in each of which he put 30 grams of substance, and sealed the tubes, placing them in a digestor so that the empty ends hung downward outside the digestor. After heating for four hours at 350°, the tubes were cooled and opened, to allow the escape of gases; then resealed and again heated. This treatment was continued till the reaction seemed finished. Triolein yielded a product of which 50 per cent. boiled below 150°; tristearin 60 per cent., oleïc acid 60 per cent., stearic acid 60 per cent. Engler found that the triolein under proper conditions left no residue, but was entirely changed into gases, water, and volatile oil.

To explain the fact that crude petroleum contains only traces of nitrogen, Engler assumes that on the decomposition of the animal remains under long continued pressure, the nitrogen escapes as ammonia, and refers to the work of Gregory[2] and Wetherill[3] on the formation of adipocere.

An objection urged against the organic origin of petroleum is that no free carbon is found in crude petroleum. Engler takes up this hitherto unanswered point and shows that if all of the oxygen of the triolein or tristearin should combine with part of the hydrogen to form water, 87 per cent. carbon and 13 per cent. hydrogen would remain.

[1] Ber. d. chem. Gesell. **20**, 595. [2] Ann. Chem. (Liebig) **61**, 362.
[3] Transactions of the Amer. Philosoph. Soc. **11**.

The numerous analyses by St. Clair Deville and Markownikoff and Oglobin, of the American, European and Caucasian petroleums show that crude petroleum contains an average of 87 per cent. carbon and 13 per cent. hydrogen—certainly a striking coincidence!

EDWARD RENOUF.

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THE CONSTITUTION OF BENZENE.

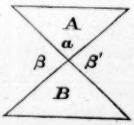
An article by H. Sachse,[1] entitled, "Ueber die Configuration des Benzolmolekülls," has recently appeared. The author comes to the same conclusion as Kékulé, viz., that the only solution of the problem can be found in a consideration of the space relations of atoms, as laid down by Van't Hoff and Wislicenus. In accordance with this hypothesis, he considers the carbon atom situated at the center of a regular tetrahedron, with its points of affinity situated at the four corners thereof, and exerting its four equal affinities in the directions of these points. He also thinks that the atoms of other elements are similarly situated at the centers of other geometrical figures, whose form is conditioned by the number and directions of the affinities of the respective atoms. If the carbon atoms of the formulas of Kékulé, Ladenburg or Claus be replaced by tetrahedrons, figures will result which will not satisfy all the conditions required by facts, and especially will they show no reason why six, and just six, such tetrahedrons should give the most stable form of combination, and why in the combination of two benzene rings, in their most stable form of combination, they should have two carbons in common, as we have in naphthalene, anthracene, and most of the high-melting products of the distillation of coal-tar. He hence concludes that there must be a union of affinities in benzene which is peculiar to this and to all rings derived from it. This condition he thinks is represented in his conception of the structure of benzene, which also gives a reason why six atoms represent the stablest form of combination, and why two rings do have two atoms in common as above stated. His conception can best be understood by the study of a model constructed as follows: An octahedron—one of pasteboard is the best—has any two of its triangular faces, which are parallel, removed. Upon each of the remaining triangular faces a tetrahedron, whose faces are of the same size as those of the octahedron, is attached, face to face. Thus a figure will result which has six free corners, one from each tetrahedron, which represent the six free affinities of benzene. An examination of this figure will show that neither the molecule nor even one carbon atom can become saturated without changing the entire system. In this respect it is like Kékulé's formula.

The six-membered ring thus formed is the most stable of all

[1] Ber. d. chem. Gesell. **21**, 2530.

rings formed of any number of carbon atoms, because each atom is so combined with its neighbor that it is in stable equilibrium, and because the system can only move as a whole, no periodic vibrations of separate carbon atoms being possible. The latter is evident from the model, and the former is proved geometrically as follows:

If $A$ and $B$ be the projection upon the plane of the paper of two tetrahedrons joined by double union as they are commonly represented according to the Van't Hoff hypothesis and as they actually occur in the model, then to be in equilibrium $\beta$ must be equal to $\beta'$, whence follows $\beta = \frac{360° - 2\alpha}{2}$, where $\alpha$ is the angle of the tetrahedron, which is 70° 32′. By substituting this for $\alpha$ in the formula, we obtain $\beta = 109° 28' = \beta'$. But this is just the angle of an octahedron, whence, as the inside of our model is an octahedron, it follows that each of the six tetrahedrons is so combined with its neighbor that $\beta = \beta'$ (the exterior and interior angles of our model) for each pair, and that they are hence in stable equilibrium.




From $\beta = \beta'$ it also follows that there is a possibility of another ring similar to our model being added to it, which must have two tetrahedrons in common with the former, as $\beta$ is the solid angle between any two of them. In this conception we have only double union of carbon atoms, which the author terms "edge-combination,"[1] as two tetrahedrons are then in combination by a common edge. This would not be possible according to our conception of the distribution of affinities in benzene, inasmuch as six carbon atoms united each by two affinities to its neighbor would leave no free affinities with which the hydrogen atoms of benzene could enter into combination. But this is where the author introduces his new conception of the union of carbon atoms peculiar to benzene and ring formation in general, above alluded to. It is this: When two carbon atoms are combined by double union, the affinity from each directed to one of the common points of union does not completely neutralise that from the other atom directed to the same point, as they meet at an angle. Hence a third affinity from a third adjacent carbon atom is used in completing the mutual neutralisation. Hence at any and every point on the model where three carbon atoms meet we have this distribution of affinities, and it is this distribution which is peculiar to ring-formation, and in particular to benzene.

For the facts which he mentions in favor of his hypothesis, reference must be made to the original article.[2] One, however, may be mentioned here, as it involves another new conception in regard to the relative distances of ortho, meta and para positions. It is the fact that ortho-dioxy-benzene compounds do not form

[1] "Kantenverbindung."

[2] Loc. cit. 2534.

anhydrides. If $x$ is the distance between any two corners of a tetrahedron, *i. e.* points of affinity, then by calculation it is found that the distance in the model between the free points of affinity of two ortho, meta or para atoms respectively is represented by

$$o = \sqrt{2}x \qquad m = 2x \qquad p = \sqrt{6}x$$

$$\text{or } o^2 : m^2 : p^2 = 1 : 2 : 3.$$

Let us apply this to the problem. The distance between the two affinities of an oxygen atom must be the same as between those of a carbon atom, *i. e.* $= x$, as is shown in compounds containing $C=O$, or carbonyl oxygen. Hence the greatest distance that an oxygen atom in combination with carbon can span, so to speak, is $x$. But according to the theory, the two ortho points of affinity must be separated by a distance represented by $\sqrt{2}x$, which is greater than $x$, and as the carbon atoms are immovable, the anhydride cannot be formed. In case of salicylic acid, where there is a side chain, bending can take place, and an anhydride, salicylide, can be formed. Sachse proposes in a later article to apply his hypothesis to addition-products, quinones, and other derivatives of benzene.

A. R. L. Dohme.

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### The Molecular Formulas of Some Metallic Chlorides and Similar Compounds.

In view of the recent developments in the study of the specific gravity of the vapors of metallic chlorides, the following article, in which a brief account is given of all such determinations which have been made, may prove of service.[1]

*Aluminium Chloride.*—In 1857, Deville and Troost[2] made five determinations of the vapor density of aluminium chloride by Dumas' method. Two at 350° gave 9.38, 9.35, and three at 440° gave 9.33, 9.34, 9.37, which correspond very well with the theoretical density 9.3 for $Al_2Cl_6$.

In 1860 Cahours[3] analysed the methyl and ethyl compounds of aluminium, and as a result proposed the formulas $Al(CH_3)_3$ and $Al(C_2H_5)_3$. The vapor densities of these compounds were determined in 1865 by Buckton and Odling,[4] using Gay-Lussac's method. One experiment on aluminium ethyl at 234° gave 4.5, the theory for $Al(C_2H_5)_3$ requiring 3.9. Two experiments on aluminium methyl at 220° and 240° gave respectively 2.8, 2.8, the theory requiring for $Al(CH_3)_3$ 2.5. Experiments ranging from 140° to 163° gave figures ranging from 4.4 to 4.1. The authors concluded that the vapor of the latter compound was anomalous.

[1] This paper was finished and in the hands of the editor of this Journal before the paper by Sidney Young on the same subject appeared in Nature (see Nature **39**, 198).
[2] Ann. chim. phys. (3), **58**, 257.
[3] Ibid. (3), **58**, 22.
[4] Ann. Chem. (Liebig), Suppl. **4** (1865), 111.

Near its boiling point, 140° C., its density corresponds to the double molecule, while above 220° it corresponds to the simple molecule.

In 1879, Victor Meyer,[1] by his own method, using an atmosphere of nitrogen, experimented on the density of aluminium chloride at 697°, but his results were uncertain, on account of the dissociation which the compound suffered. He suggested that this difficulty might be overcome by using an atmosphere of chlorine.

In 1887,[2] Nilson and Petterson, by Meyer's method, working in nitrogen at 440° and 458°, obtained respectively 7.79 and 4.8. Between 458° and 943° the result remained practically 4.5, which is very close to 4.6 required for $AlCl_3$. Above 943° dissociation was observed, the vapors attacking the platinum vessel.

In 1888, Friedel and Crafts,[3] by Dumas' method, made 21 determinations of the vapor density of aluminium chloride, under variations of temperature and pressure. Twelve experiments at 760 mm. between 218° and 400° gave an average result of 9.36; five at 1520 mm. and below 400° gave an average of 9.32. The remaining experiments made above 400° gave 8.6, which the authors attributed to dissociation. They also suggested that dissociation is favored by the use of inert gases in Meyer's method.

The work on the hydrocarbon compounds of aluminium was taken up again by Roux and Louise[4] in 1888. Using Meyer's method with nitrogen, they made two experiments on aluminium methyl at 182° and obtained 5.08 and 5.15, the theory for $Al_2(CH_3)_6$ requiring 5.02. Two experiments at 216° gave 4.78 and 4.7; two at 350°, 2.33 and 2.55; two at 440°, 1.94 and 1.68. The authors claim that the compound vaporises undecomposed at 182°, 42° above the boiling point, but at higher temperatures dissociates. Similar results were reached with the ethyl compound. At 235°, 35° above the boiling point, 8.15 and 7.99 were obtained in two determinations. The theory for $Al_2(C_2H_5)_6$ requires 7.92. At 258° three experiments gave 6.41, 6.35 and 6.04; at 310°, 2.1; at 440°, 1.3. Above 250° dissociation occurred. Several determinations were made by Raoult's method, using ethylene bromide as the solvent. Three results obtained with the ethyl compound gave 240, 234 and 229 for the molecular weight, figures which are fairly near 229 required for $Al_2(C_2H_5)_6$. The results obtained with the propyl and isoamyl compounds were very discordant, in consequence, no doubt, as claimed by the authors, of the presence of impurities.

The work done by Deville and Troost[5] in 1857 on aluminium bromide and iodide has not been repeated. Their results, 18.62 and 27, agree fairly well with 18.51 for $Al_2Br_6$ and 28.3 for $Al_2I_6$.

[1] Ber. d. chem. Gesell. **12**, 1199.
[2] Compt. rend. **106**, 497.
[3] Ztschr. phys. Chem. **1**, 459.
[4] Bull. Soc. chim. (Paris), 1888, 497.
[5] Ann. chim. phys. (3) **58**, 257.

*Beryllium Chloride.*—In 1884, Nilson and Petterson,[1] working by Meyer's method in carbon dioxide, made a series of experiments between 686° and 812°. The densities found varied from 2.75 to 2.93. In 1885[2] a more extended series was made, varying from 686° to 1502°, giving densities varying from 2.7 to 2.85. The theory for $BeCl_2$ requires 2.77.

*Chlorides of Chromium.*—The only work done on these compounds is that by Nilson and Petterson,[3] 1888. The trichloride volatilises normally between 1190° and 1277°, giving an average density of 5.5, the theory for $CrCl_3$ requiring 5.48. Above 1300° dissociation was observed. The dichloride was very difficult to volatilise. From 1300° to 1400° the density 7.8 was found; at 1500°, 7.3; and at 1600°, 6.23. The authors think the theory 4.26 for $CrCl_3$ may be reached at higher temperatures.

*Cuprous Chloride.*—In May, 1880, V. and C. Meyer[4] tried the vapor density at a bright red heat and found it to be 7.05, the theory for $Cu_2Cl_2$ requiring 6.84. The scientific world questioned this result, so in June[5] of the same year the experiment was repeated at 1560° and the figure 6.93 obtained.

*Ferrous Chloride.*—Victor Meyer, 1879,[6] using his own method with nitrogen, made some experiments on ferrous chloride at a temperature not given, and found that the salt broke up into the metal and ferric chloride. He suggested that in an atmosphere of hydrochloric acid gas this would not occur, and in 1884[7] made the determination at a bright yellow heat. Two densities were found, 6.67 and 6.38, lying midway between 4.39, the theory for $FeCl_2$, and 8.78 for $Fe_2Cl_4$. There was no dissociation.

In 1888, Nilson and Petterson,[8] by Meyer's method, made a series of experiments between 1300° and 1500°, and obtained densities varying from 4.34 to 4.30.

*Ferric Chloride.*—In 1860, Deville and Troost[9] made two determinations of the vapor density of ferric chloride by Dumas' method, in a bath of sulphur, obtaining the figures 11.37 and 11.42. Theory for $Fe_2Cl_6$ requires 11.27.

Victor Meyer,[10] in 1879, made the same determination by his own method, in an atmosphere of nitrogen. At 448° he obtained 11.14, and at 619°, 11.01. Dissociation was observed at higher temperatures. In 1888 he and Grünewald[11] repeated the work, making twenty-two determinations in an atmosphere of nitrogen, and four in chlorine. At 448° four experiments in nitrogen gave an average of 10.49, and two in chlorine gave 10.65. Three experiments in nitrogen at 518° gave an average of 9.57. At the same time, however, the salt had decomposed, yielding 10 per cent. of ferrous chloride. Two experiments in chlorine at the same temperature gave an average of 8.74. In nitrogen, as the

[1] Ber. d. chem. Gesell. **17**, 987. [2] J. prakt. Chem. **33**, 13. [3] Ztschr. phys. Chem. **12**, 674.
[4] Ber. d. chem. Gesell. **13**, 1116. [5] Ibid. **13**, 1283. [6] Ber. d. chem. Gesell **12**, 1199.
[7] Ibid. **17**, 1335. [8] Ztschr. phys. Chem. **2**, 671. [9] Ann. chim. phys. (3), **58**, 283.
[10] Ber. d. chem. Gesell. **12**, 1199. [11] Ber. d. chem. Gesell. **21**, 687.

temperature rose above 518°, the dissociation increased correspondingly, reaching 33 per cent. at about 750°. Nevertheless the authors conclude, especially from the results in chlorine, that the molecule $Fe_2Cl_6$ does not exist.

Friedel and Crafts[1] were engaged on the same problem in 1888, under the influence of diminished pressure and low temperature. Between 356° and 442° several experiments in chlorine and at 760 mm. gave densities varying from 11.30 to 12.04. At 325° and 407.4 mm., 12.47, and at 321° and 377.4 mm., 11.41. Dissociation was not observed in any of the work. In an atmosphere of nitrogen, however, at 760 mm., dissociation occurred at 433° and 432.7°, giving 10.75 and 10.97.

*Gallium Trichloride.*—In 1880, Lecoq de Boisbaudran,[2] by Dumas' method, determined the vapor density at 440°, 357°, 273°, and 247°, to be respectively 7.8, 10, 11.9 and 13.4. The theory for $Ga_2Cl_6$ is 12.16. Friedel,[3] in 1881, by Meyer's method at 440°, 357° and 440°, found 7.8, 8.5 and 6.6. In 1888, Friedel and Crafts[4] repeated the work in nitrogen and under increased pressure. At 307° and 760 mm. they obtained 10.6; at 357° and 760 mm., 9.1; at 377° and 1090 mm., 7.8; at 237° and 1138 mm., 11.73. Dissociation was observed at higher temperatures.

In 1888, Nilson and Petterson,[5] by Meyer's method, at 350° obtained 8.85; between 440° and 606°, 6.12 and 6.14 were obtained, but at higher temperatures the salt decomposed. They throw out the figure obtained at 350° and conclude that the two results obtained at 440° and 606° settle the question as to the molecular weight.

At the same time they prepared some gallium dichloride and determined its vapor density. Between 1000° and 1100° they obtained 4.8. The calculated figure for $GaCl_2$ is 4.86. Above 1300° the salt decomposed.

*Chlorides of Indium.*—In 1879, Victor Meyer[6] determined the density of the vapor of the trichloride to be 7.87. The theory for $InCl_3$ is 7.55. At the bright red of the experiment no dissociation was observed.

Although other chlorides were believed to be possible, the trichloride was the only one known until 1888. In that year Nilson and Petterson[7] showed the existence of the dichloride and the monochloride. The vapor densities of the three chlorides were taken by Meyer's method. The trichloride between 606° and 850° gave figures varying from 8.16 to 7.39; and between 1048° and 1200°, 6.72 to 6.23. The fall in density was attributed to dissociation above 1000°. The dichloride between 1167° and 1400° gave 6.55–6.43, figures which agree very well with the theory for $ICl_3$, which is 6.36.

The monochloride between 1100° and 1400° gave 5.3–5.5, the theory for ICl being 5.14.

[1] Compt. rend. **107**, 301. [2] Compt. rend. **93**, 326. [3] Loc. cit. [4] Ibid. **107**, 306.
[5] Ztschr. phys. Chem. **2**, 666. [6] Ber. d. chem. Gesell. **12**, 611. [7] Ztschr. phys. Chem. **2**, 650.

*Stannous Chloride.*—In 1870,[1] Reith, using a Hofmann's furnace, made two experiments on the vapor of stannous chloride (temperature not mentioned), and obtained 7.47 and 6.88. The theory for $SnCl_2$ is 6.53. In 1879, V. and C. Meyer,[2] in two determinations by Meyer's method at 619° and 697°, found 12.85 and 13.08, which agree very well with 13.06, the theory for $Sn_2Cl_4$.

V. Meyer and Züblin[3] repeated the experiments in 1880 and found at 800°, 7.22; at 880°, 6.67; and at 970°, 6.23. The glass vessel was attacked by the vapors, but no dissociation was observed. The authors suggested the existence of two modifications of the compound. Between 619° and 697° the vapor density leads to the molecular weight for $Sn_2Cl_4$, and this breaks down to two molecules of $SnCl_2$ between 800° C. and 970° C.

Biltz and Meyer[4] repeated these experiments in 1888, this time using an atmosphere of nitrogen. Five determinations were made at small intervals of temperature between 639° and 790°. They obtained the following figures: 8.76, 8.57, 8.49, 8.26, 7.7. The sixth experiment was made at 1113° and gave 7.1. The gradual sinking of the density without dissociation of the gas led the authors to assume that at a higher temperature the theory for $SnCl_2$, 6.53, would be reached.

*Thorium Chloride.*—From analyses of potassium thorium sulphate, Berzelius in 1827 assumed the formula of the oxide to be ThO. In 1852, Bergmann wrote the formula $Th_2O_5$, because of similarities to zirconium oxide, which he regarded as a sesquioxide $Zr_2O_3$. In 1857, however, Deville and Troost[4] showed that from the density of the vapor of zirconium chloride, its oxide should be written $ZrO_2$. Rammelsberg in 1860, and others later, showed that from the many analogies of the oxide of thorium to the oxides of silicon, titanium, and tin, its formula must be $ThO_2$. In 1885, Troost[5] determined the vapor density of the chloride of thorium by Meyer's method, using a bath of zinc. Three trials gave 5.9, 7 and 7.09. The theory requires 12.93 for $ThCl_4$. In 1887, Krüss and Nilson[6] repeated the experiments by Meyer's method, in an atmosphere of carbon dioxide. Between 1000° and 1270° figures varying from 11.2 to 12.4 were found. At 1400° dissociation was observed.

P. S. Baker.

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### Grünwald's Mathematical Spectrum Analysis.

Dr. Anton Grünwald, Professor of Mathematics in the Technical High School at Prague, has given his theory of spectrum analysis in the following papers: (1) Ueber das Wasserspectrum, das Hydrogen- und Oxygenspectrum: *Astronomische Nachrichten*, No. 2797, 1887, and Phil. Mag. **24,** 354, 1887; (2) Math.

[1] Ber. d. chem. Gesell. **3,** 618. [2] Ibid. **12,** 1195. [3] Ber. d. chem. Gesell. **13,** 811.
[4] Compt. rend. **45,** 824. [5] Ibid. **101,** 360. [6] Ztschr. phys. Chem. **1,** 305.

Spectralanalyse des Magnesiums und der Kohle: *Monatshefte für Chemie* **8**, 650; Wiener Sitz. Berichte, II Abth. **96**, 1887; Phil. Mag. **25**, 343 (1888), (abstract); and (3) Math. Spectralanalyse des Kadmiums: *Monatshefte für Chemie* **9**, 956.

His aim is to discover relations between the elements by tracing connections between their spectra, and thus to arrive at simpler, if not fundamental "elements." He considers the lines in the spectra of two substances, say $A$ and $B$. If he finds a group of lines in the spectrum of $A$ which, on multiplication with a simple numerical factor, gives line for line a group in the spectrum of $B$, he assumes that $A$ and $B$ have a common component. This factor which transforms the one group into the other is, he says, the ratio of the volumes occupied by the common constituent in unit volume of the two substances. Thus, let $c$ be common to $A$ and $B$, and let it occupy the volume $[a]$ in unit volume of $A$, and $[b]$ in unit volume of $B$; then the factor which transforms that part of the spectrum of $A$ due to $c$ into that of $B$ also due to $c$ is $[b]/[a]$.

It is not difficult to find relations between the spectra of different substances; and, accepting Dr. Grünwald's hypothesis as to the transforming factor, we can deduce formulas for the elements. For example, in the hydrogen spectrum there are two groups of lines, $[a]$ and $[b]$, which, when multiplied respectively by $\frac{1}{30}$ and $\frac{4}{5}$, give corresponding groups in the spectrum of water, and, since in water hydrogen occupies $\frac{2}{3}$ of the volume, we have the equations:

$$[a] + [b] = 1$$
$$\tfrac{1}{30}[a] + \tfrac{4}{5}[b] = \tfrac{2}{3}$$
$$\therefore \quad [a] = \tfrac{4}{5}, \quad [b] = \tfrac{1}{5},$$

which gives hydrogen the composition $ba_4$. For reasons which depend upon solar physics, Grünwald calls the substance $a$ coronium, and $b$ helium. Further, he says that all the lines in Hasselberg's secondary spectrum of hydrogen can be changed into water-lines by multiplying by $\frac{1}{2}$; which shows, according to his theory, that the modified molecule H′ occupies in $H_2O$ half the volume it does in the free condition. He finds that oxygen has the composition $H'b_4(b_4c_5)_5$, where $c$ is a new substance. In his last paper, however, Dr. Grünwald states that he has proved $c$ to be nothing but $a$ in a different state of compression.

He adopts the spectrum of water, *i. e.* of the oxyhydrogen flame, as a standard, and is then able to give various criteria by means of which the primary elements $a$ and $b$ may be recognised. Among them are the following: If $\lambda$ is the wave-length of any line produced by $a$ as it exists in hydrogen, $\frac{1}{30}\lambda$, $\frac{3}{4}\lambda$, $\frac{4}{75}\lambda$ will each be the wave-length of a line of the water-spectrum; and if $\lambda$ is the wave-length of any line produced by $b$ as it exists in hydrogen, $\frac{4}{5}\lambda$ will be the wave-length of a line of the water-spectrum. Applying his criteria to magnesium, carbon, and cadmium, he finds that they are made up entirely of $a$ and $b$ in various states of com-

pression. For instance, one group of lines in the cadmium spectrum is transformed into a group of *b* by the factor $\frac{1}{2}$, another group is identical with a group of *b*, and so on. But the group of lines of *shortest* wave-length is transformed into a group of *b* by the factor $\frac{7}{8}$; and cadmium falls in the 7th row of Mendelejeff's Table. Similarly, the group of lines of shortest wave-length of zinc is transformed into a group of *b* by the factor $\frac{5}{6}$, and zinc is in the 5th row of the table. Dr. Grünwald finds in this a general law which he verifies in the cases of Al, Si, Fe, Cu, Zn, As, Sr, Ag, Cd, In, Sn, Sb, Te, Ba, Au, Hg, Tl, Pb and Bi. He further connects the lines of greater wave-length with the substance *a*; and, as in all cases so far tried all the lines can be deduced from these two substances, he is led to believe that *all the so-called elements are compounds of the primary elements a and b.*

It is unfortunate that Dr. Grünwald has not published a complete list of the lines characteristic of *a* and *b*, for until this is done his theory cannot be accurately tested. There are two distinct questions to be answered: (1) Are there any numerical relations connecting the spectra of the elements? and if so, (2) What is the meaning of the fact? Cornu, Deslandres and others have long since answered the first question for us, but whether Dr. Grünwald's answer to the second one is correct or not depends upon the completeness with which the numerical relations hold for the *entire* spectra of the substances. It is here that Dr. Grünwald's work can be criticised.

As noted above, the spectrum of the oxyhydrogen flame is used to test the existence of lines belonging to *a* and *b*. By far the most accurate and complete determination of this spectrum is that of Liveing and Dewar (Phil. Trans. 1888); but this does not always answer Dr. Grünwald's purposes. In the B. A. report for 1886 there is a provisional list of lines of the water-spectrum, which he often uses, although the wave-lengths have since been corrected. Further, if other lines are necessary, they are found by halving the wave-lengths of the secondary spectrum of hydrogen. Many lines thus determined are actually present in the water-spectrum; but why are not *all* there? Dr. Grünwald says it is because the amplitude of vibration of parts of the molecule can be so changed, owing to the presence of other substances, that the intensity may increase or diminish, or become too faint to be observed. To this argument there is absolutely no answer. In some cases, too, the average of two wave-lengths is used as a criterion of a wave-length of *b* which falls between them! And as a last resort, if the necessary wave-length cannot be found in the water-spectrum by any of these means, it is put down as "new" and is called an "unobserved" line. As just shown, Dr. Grünwald easily explains why the strongest lines in the spectrum of an element, cadmium for example, when "transformed" into water-lines, may be faint; and *vice versa.* But how does he account for

the fact that double lines are not transformed into double lines? This seems to me a fundamental objection. The concave-grating gives the only accurate method of determining the ultra-violet wave-lengths of the elements; and, as a consequence of not using it, most of the tables of wave-lengths so far published are not of much value. So Grünwald's error here may be great. And, besides, when we consider that in the water spectrum as given by Liveing and Dewar, without the help of the secondary spectrum of hydrogen, there is on the average one line for every two Angström units, it would be remarkable indeed if any law could not be verified. This is strikingly shown in the first group of the cadmium lines. Here 6742 and 6740 are two readings for the wave-lengths of the *same* line, as made by two observers; yet Grünwald finds a water-line for each of them!

The fact that there are exact numerical relations connecting the spectra of different elements does not afford a proof of Grünwald's hypothesis; and, until the above difficulties are removed, the evidence is against it. But, even granting it, how do we know that *a* and *b* are not themselves compounds? In the "second group" of cadmium lines there are 19 lines which can be transformed into *b* lines; *b* has many other lines; so at the most this shows only that cadmium and *b* have a common constituent, unless, of course, the absence of the other cadmium lines is accounted for in Grünwald's own way of varying intensity.

The lines of the spectrum of any one substance, as carbon or iron, seem to fall into definite series or groups; and the wave-lengths of the lines in these groups can be expressed by formulas, as is well known. All that the fact of there being a connection between the spectra of different substances seems to show is, then, that there may be a formula common to many elements, as Kayser and Runge have recently found. And all that this means is that the molecules of these elements vibrate in general according to a similar law.

JOSEPH S. AMES.

PHYSICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

## NOTES.

### *Boric Acid.*

As is well known, in any family of base-forming or positive elements, the positive character grows less marked as the atomic weight decreases. Considering the position of boron in the periodic system, at the head of the aluminium family, and considering, further, the fact that aluminium hydroxide is a weak base,

we should expect to find that the corresponding hydroxide of boron has but slight basic properties. That it is not entirely devoid of basic properties is shown by the existence of the phosphate, $BPO_4$; the sulphate, $B_2(SO_4)_2.H_2O$; and a compound analogous to tartar-emetic in which boron takes the place of antimony.

A strong argument in favor of the view that boron and aluminium are closely related elements is found in the isomorphism of euclasite and datholite. The analogy in composition between these minerals is shown by the formulas:

$2BeO.Al_2O_3.2SiO_2.H_2O$ .... Euclasite
$2CaO.B_2O_3.2SiO_2.H_2O$ ..... Datholite.

Attention has recently been called to the facts above-mentioned by P. Georgievic, who is engaged upon an investigation of boric acid, particularly with reference to the relative strength of the acid. He also calls attention to the following points:

1. Solutions of alkali carbonates and bicarbonates are not changed by boric acid. Although this fact has long been known to those engaged in the manufacture of borax, it is not mentioned in any text-book of chemistry.

2. A solution of borax absorbs such large quantities of carbon dioxide when this gas is conducted into it, that the boric acid is in all probability entirely replaced. Further, barium borate suspended in water is completely dissolved in a few minutes by passing hydrogen sulphide through the liquid.

3. When boric acid is added to a solution of potassium iodide and iodate, or of potassium iodide and nitrite, not a trace of iodine is set free.

4. The dark red color produced by adding ferric chloride to a solution of an acetate does not disappear on adding boric acid. The same is true of the purple color caused by bringing phenol and ferric acetate together.

Finally, the author suggests that the avidity of boric acid as given by Ostwald, viz., 0.01, is probably too high, for the reason that acetic acid, to which is ascribed the avidity 0.03, has the power to set iodine free when applied as directed under 3 above; and, further, when an acetate is used and boric acid added, iodine is not set free.—(*Journal für praktische Chemie* **38**, 118.) I. R.

## *Hydrazine.*

In the course of investigations on the diazo- and azo-compounds of the fatty series, Th. Curtius and J. Lang[1] have shown that when the ethyl salt of diazo-acetic acid, $CHN_2.CO_2C_2H_5$, is treated with a concentrated aqueous solution of caustic alkali, a salt of triazo-acetic acid, $C_3H_3N_6(COOH)_3$, is formed. This acid is stable in the free condition, and when boiled with mineral acids it gives

[1] J. prak. Chem. [2] **38**, 521.

up its nitrogen in the form of hydrazine, $N_2H_4$. The main reaction involved is that represented in the equation:

$$C_3H_3N_3(COOH)_3 + 6H_2O = 3C_2O_4H_2 + 3N_2H_4.$$

The oxalic acid which is the other product of the reaction is, however, more or less completely transformed into carbon dioxide and formic acid, a fact which is expressed in this equation:

$$C_3H_3N_3(COOH)_3 + 6H_2O = 3CO_2 + 3HCOOH + 3N_2H_4.$$

Hydrazine is formed also by the following reactions:

1. By reduction of ethyl diazo-acetate by zinc-dust and acetic acid,[1] or by aluminium or zinc filings in alkaline solution; and

2. By boiling with water the addition-products which the ethereal salts of diazo-acetic acid form with the ethereal salts of unsaturated acids.

The decomposition of triazo-acetic acid is, however, by far the best method for preparing hydrazine. The yield is about 90 per cent. of the theoretical.

Th. Curtius and R. Jay[2] have made hydrazine and its derivatives the subject of an extensive investigation, the results of which are briefly summarised in this note. As regards the quantities with which they worked, an experiment is described in which they treated 245 grams of triazo-acetic acid in 2 liters of water with 300 grams of pure concentrated sulphuric acid. On cooling, pure hydrazine sulphate was deposited in colorless crystals. On evaporating the mother-liquor, a second deposit of the sulphate was obtained. From the last mother-liquors the remaining hydrazine was extracted by shaking with benzoic aldehyde, with which it forms an insoluble compound of the formula $N_2(CH.C_6H_5)_2$, called benzalazine. From benzalazine the hydrazine is then obtained by treating with sulphuric or hydrochloric acid:

$$(C_6H_5CH)_2N_2 + 2H_2O + H_2SO_4 = 2C_6H_5CHO + N_2H_4.H_2SO_4.$$

Hydrazine combines with one or two molecules of monobasic acids to form stable salts. Even in acid solution these have extraordinary reducing power, the products of the action being nitrogen and water. When heated alone they decompose at a high temperature, forming ammonium salts, nitrogen and hydrogen. When a nitrite is added to hydrazine salts, nitrogen is rapidly evolved. Of the salts thus far examined, only the sulphate is difficultly soluble in water. The salts are either insoluble or but slightly soluble in alcohol. Some of them crystallise very well, and most of them appear to be isomorphous with the corresponding ammonium salts. The physical properties of hydrazine itself are as yet unknown. It appears from what has thus far been learned that it is a gas or a liquid boiling at a low temperature. That its molecular weight is correctly represented by the formula $N_2H_4$ follows from the existence of the two hydrochloric acid salts, $N_2H_4.HCl$ and $N_2H_4.2HCl$, and also from the results obtained in determining

[1] J. prak. Chem. [2] **38**, 440. [2] Ibid. [2] **39**, 27.

the molecular weight of benzalazine by Raoult's method. The compound has a remarkable affinity for water, and forms a hydrate of the composition $N_2H_4 + H_2O$. As, in setting hydrazine free from its salts it is necessary to use the oxides or hydroxides of the alkali metals or of the metals of the alkaline earths, and as water is necessarily formed in the reaction, thus:

$$N_2H_4(AH)_2 + M_2O = N_2H_4 + H_2O + 2MA,$$

it follows that hydrazine is always obtained in the form of the hydrate. An attempt was made to break up this hydrate by distilling a mixture of hydrazine dichloride and quicklime from a silver vessel, and passing the volatile product through a silver tube filled with pieces of quicklime. No gas was obtained, and only a small quantity of a liquid came over. This proved to be hydrazine hydrate. It was shown further that barium oxide has not the power to decompose hydrazine hydrate into water and hydrazine. A large quantity of the hydrate has been made by distilling the sulphate with potassium hydroxide from silver vessels, and fractioning the distillate. Details in regard to this remarkable compound will be given in a later article by Curtius and Schulz. Meanwhile the following is all that is said concerning it. It has the composition $N_2H_4 + H_2O$, and forms a colorless, inodorous liquid with a high refracting power, which fumes in the air and boils without change at 119°. Pure hydrazine hydrate does not change in closed vessels. At the boiling temperature it attacks glass strongly, and destroys cork and rubber. It has an alkaline taste, and leaves upon the tongue a burning sensation. It is an extremely active poison for lower organisms.

Hydrazine is the strongest reducing agent known. A neutral solution of platinic chloride is reduced to metallic platinum, which separates in beautiful pieces having a silver luster, or in the form of a mirror. In acid solution, on the other hand, platinic chloride is reduced only to platinous chloride. In the same way hydrazine hydrate precipitates all easily reducible metals in the cold. Silver separates in compact lustrous pieces, apparently of crystalline structure. With very dilute solutions most perfect mirrors of great beauty are obtained. From aluminium the hydroxide is precipitated; and chromic hydroxide is precipitated from solutions of chromates. With mercuric chloride there is first formed a yellow-colored double salt, from which metallic mercury soon separates. In acid solution ferric chloride is reduced to ferrous chloride, and cupric to cuprous chloride. Dropped upon mercuric oxide or quinone, hydrazine hydrate causes an explosion. The facts mentioned show that this substance is undoubtedly destined to play an extraordinarily important part in analytical chemistry, and extensive investigations are now in progress with reference to its applications in this field. J. R.